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CARBON NANOTUBES FILLED POLYURETHANE NANO-COMPOSITES: A FILLER MORPHOLOGY AND SURFAC-TANT STUDY

Master of Science Thesis

Examiners: Professor Jyrki Vuorinen

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Abstract

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Carbon nanotubes (CNT) filled nanocomposites have gained much attention due to their excellent electrical and mechanical properties. The excitement related to such materials seems to be ever increasing as they have already proved their significance in many applications including sports, automotive, aeronautical and electronics industry. However, commercialization has been rather slow due to challenges imposed on developing a new technology. Nevertheless, CNTs are predicted to commercialize to a significant extent in next decade, which can be attributed to crossing barriers such as standardizing bulk production and effective processing methods for nanocomposites. Latex technology has emerged as one of these methods and have shown potential by providing a relatively simple pathway to produce finely dispersed nanocomposites.

The main aim of this thesis is to examine the effect of CNT morphology on mechanical and electrical properties of CNT filled nanocomposites. It also addresses the surfactant aspect of latex technology and proposes an approach to make it more eco-friendly by eliminating the use of environmentally toxic surfactants. Latex technology was used to prepare polyurethane nanocomposites. CNTs were dispersed in aqueous surfactant solution with the aid of ultrasonic energy to produce CNT dispersions; which were further mixed with polymer latex and casted into nanocomposite films.

The results of this study suggests that aspect ratio of CNTs is more accurate parameter for characterizing the mechanical properties. On the other hand, electrical properties are more dependent on length of CNTs. The results of surfactant study, for the first time, suggest that Dabco DC 193 is an efficient surfactant for dispersing nanotubes in water. DC193 has indicated to have potential as an eco-friendly alternative to Triton X-100; a popular surfactant which is toxic to the environment. Results drawn in this work provides lucid understanding to behaviour of CNTs in polymeric matrix, which are likely to contribute towards commercialization of latex technology.

Preface

The work reported in this thesis was conducted at the Department of Materials Science, Tampere University of Technology, Finland during September 2013 – February 2014. This research is the result of collaboration between Plastics and Elastomers laboratory at Tampere university of Technology with Department of Materials Science, Oxford University under the CONTACT project.

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To my parents, thank you for your support and motivation. I am truly blessed to have such a wonderful role models. A big thanks to all my friends for their support and motivation during this period. Finally, I express my gratitude to all my teachers for all the valuable lessons they have taught me.

Tampere, 10 December 2014

Jatin Sethi

Contents

List of symbols and abbreviations

a1,a2	unit vectors in CNT's lattice
Δ	phase angle
m, n	number of steps along CNT's unit vectors
Θ	chiral angle
Φc	volume fraction
Tg	glass transition temperature
δ_d, δ_p, δ_h	Hansen solubility parameter
E	young's modulus
C_h	chiral vector
P	electrical resistivity
C150P	baytubes c150p
CNTs	carbon nanotubes
CCVD	catalytic carbon vapour deposition
CVD	chemical vapour deposition
CTAB	hexadecyltrimethyl- ammoniumbromide
DMA	dynamic mechanical analysis
DMF	dimethyl formamide
DTAB	dodecyltrimethyl-ammoniumbromide
FTIR	fourier transform infrared spectroscopy
GNP	graphene nanoplatelets
HSPs	hansen solubility parameters
NC 7000	nanocyl nc 7000
MEK	methyl ethyl ketone
MFFT	minimum film forming temperature
MMT	organomodified montmorillonite
MWCNTs	multi walled carbon nanotubes
NIR	near infra red flourscence
NMP	N-metyl pyrollidone
OPE	octylphenol ethoxylates
OLED	organic light emitting diodes
PEPU	polyester-polyurethane
PU	polyurethane
SEER	salt-enhanced electrostatic repulsion
SEM	scanning electron microscopy
SDBS	sodium dodecyl benzenesulfonate
SDS	sodium dodecyl sulfate
SWCNTs	single wall carbon nanotubes
TEM	transmission electron microscopy
TGA	thermo gravimetric analysis
TTAB	tetradecyl trimethyl ammonium bromide
TX100	triton x 100 surfactant
Vdw	van der waals forces

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1 Introduction

CNTs are seamless hollow cylinders of one or many perfect graphite sheets. They were accidentally discovered by Dr. Sumio Iijima in 1991. Since their discovery, CNTs have gained a special attention due to their extra-ordinary mechanical, electrical and thermal properties [1]. Their popularity arises from their miniscule size (of nanometre range), which is comparable to polymeric chains used in composite matrices [2]. The small size and functional properties of CNTs provides significant advantages over conventional fibers and fillers used to prepare composites. In the recent years, a lot of research has been focused on preparing and characterizing CNT-filled nanocomposites. Such materials are already being used in various commercial applications such as anti-fouling coatings, automotive parts and sporting goods [3]. When compared to the amount of research done on this topic in last two decades, the extent of commercialization is not satisfactory.

Polymer based nanocomposites are one of the most desired use of CNTs. They can be used for industrial applications like static dissipative or conductive parts in automotive or electronic industry [4]. CNTs are used as conductive fillers as they are inherently conductive in nature, having current carrying capacity almost 1000 times the copper wires (on the basis of surface area) [5]. Additionally, CNTs have reported to enhance mechanical properties substantially; however, such occurrences are rather rare [6], [7]. In order to achieve the enhanced properties; the nanofiller should be finely dispersed in polymer. However, achieving a fine dispersion in nanocomposite is a challenging task; CNTs are commercially supplied in the form of aggregated bundles, which are formed due to high aspect ratio and presence of strong van der Waals (vdw) attraction among them. The magnitude of these forces can be as high as 500 eV/μm for single walled CNTs [8], which makes it difficult to separate CNTs at individual level and achieve a fine dispersion. It is also a major barrier in the way of commercial success of CNT filled nanocomposites.

Numerous methods are available for preparing CNT filled polymeric composites; most popular ones are solution processing, melt processing and in-situ polymerization [9]. Solution processing has been known for producing well dispersed nanocomposites [10]–[14]; in this method, polymers are dissolved in solvents and CNTs are incorporated in polymer solution, which can be later casted to obtain a nanocomposite. The choice of solvent is critical for this method. Dimethylformamide (DMF), chloroform and N-methylpyrrolidone (NMP) are the most effective organic solvents known for dispersing CNTs [15]. However, there are certain disadvantages arising from use of organic solvents as dispersion medium. DMF and chloroform are carcinogenic to humans and

NMP evaporates extremely slowly and gets trapped on polymer carbon nanotube interfaces, which results in diminished properties [16]. Additionally, the usage of organic solvents leads to fire hazards and work safety precautions, which needs to be followed in order for safe handling and storage.

For this reason, researchers have shown an increased interest in techniques that can replace organic solvents with water as dispersion medium. The process benefitting from water as dispersion medium is termed latex technology. Using water instead of organic solvents is indeed lucrative, as it is an environment friendly alternative. Moreover, water is inexpensive, universally available and can be easily obtained in ultrapure form. However, there are challenges needed to be overcome for creating a stable dispersion of CNTs in water. CNTs are inherently hydrophobic in nature as water creates a contact angle of 80-90° on graphene layers [17]. Hence, CNTs dispersed in water are aggregated almost instantly when sonicated. However, surface modified CNTs are known to produce stable suspensions in water. Surface modification (or functionalization) of CNTs can be classified into two categories: covalent and non-covalent methods [18]. Covalent methods include functionalization through various chemical reagents. It is worth mentioning that chemical functionalization disrupts the flow of π electrons, which leads to diminished electrical and thermal properties [2], [19]. On the other hand, non-covalent method results in chemical moieties such as surfactant molecules and deoxyribonucleic acid (DNA) attaching to the surface of CNTs. Non covalent method is considered superior as it causes no change in π-electron cloud of graphene layers, and thus causing no harm to electrical and thermal properties of nanotubes [6], [18], [20].

CNT filled nanocomposites are highly desired for their electrical conductivity. CNTs offers a huge advantage compared to conventional fillers such as carbon black. With CNTs, a percolation threshold can be achieved at lower concentration (less than 5wt% - depends on processing method) [21]. On the other hand, carbon black is needed in high concentration (approximately 25 wt%) [22]. Such a high amount of filler results in stiffening of composites, thus making it brittle and unsuitable for many applications.

In the recent years, lot of research has been focused on studying the percolation threshold of fillers and resulting electrical properties of nanocomposites. It has been reported that aspect ratio is one of the important parameter in determining the percolation threshold [23]–[28]. On the other hand, some researchers have reported length as a critical factor in determining the percolation threshold [29], [30]. However, analysis of data on the basis of aspect ratio can be misleading as aspect ratio is relative quantity. It is possible that two different types of CNTs have same aspect ratio and different length (and diameters too). Therefore, length might play an important role in final properties. Moreover, it has been mentioned by Lima et al. that longer CNTs will result in lower percolation threshold in comparison to shorter ones [31]. It can be easily imagined that among two different CNTs of same aspect ratio, longer nanotubes will easily form an

interconnected network in matrix. Additionally, longer CNTs will have less number of contacts and therefore, will have less magnitude of contact resistance resulting in improved electrical conductivity. Therefore, a confusion exists and need of study arises that simultaneously evaluates the effect of length and aspect ratio on electrical properties of nanocomposites.

On the other hand, aspect ratio has been proven to be more reliable parameter for mechanical properties [27], [28], [32], [33]. However, to the best of author's knowledge, no study has been found that simultaneously evaluates the effect of aspect ratio and length on mechanical properties. Moreover, a large number of studies on effect of CNT morphology (aspect ratio, length) on properties of nanotubes reinforced composites have not considered the effect of processing method on CNTs [26], [28], [34]–[36]. Commonly used processing methods such as sonicating and melt processing are known to shorten the CNTs and thus leading to reduced aspect ratio [37], [38]. Therefore, a detailed study is required that evaluates the impact of actual morphology on the performance of nanocomposites.

Another important aspect of latex technology is use of ultrasonic energy to disperse nanotubes. CNTs are commercially supplied in form of bundles, which are formed due to presence of high magnitude of vdw forces [8]. Sonication is an effective and most frequently used technique in dispersing carbon nanotubes [19], [39]–[41]. However, it has been reported that CNTs deform and shorten, when subjected to sonication in liquid medium [37], [42], [43], which significantly affects the electrical and mechanical properties of nanocomposites. Therefore, aggressive sonication (high power sonication) should be avoided during processing [44]. Grossiord et al. have reported that power of approximately 20 watts is enough to disperse CNTs [45], which is relatively low in comparison to power used by other researchers [8].

This thesis also focuses surfactant aspect of latex technology. It is worth mentioning that most popular commercial surfactants such as octylphenol ethoxylates (OPEs) are extremely harmful to the environment, particularly aquatic one. Additionally, they might also mimic the behaviour of animal hormones and act as endocrine disruptor [46]. In Europe, OPEs are listed as "priority hazardous substance" under Water Framework Directive. On international level, use of OPEs is recommended to be phased out under OSPAR convention. Furthermore, under Helsinki convention, OPEs are listed as substance of priority action [47]. Triton X-100 (TX100), which is reported as one of the most suitable and highly efficient surfactant for preparing CNT filled nanocomposites [18], [48], belongs to OPE class of surfactants. In fact, other grades of Triton are also listed as effective dispersants such as Triton X-405 [39], [49]. Therefore, there is a need to find more suitable eco-friendly surfactant that can replace such hazardous surfactants.

1.1 Aim and structure of thesis

This thesis is divided into two research studies: The first study focuses on understanding the influence of CNT morphology on electrical and mechanical properties of nanocomposites. It also aims to establish, which one among aspect ratio and length is critical parameter in determining the properties of nanocomposites. Three type of MWCNTs of different aspect ratio were selected: two of them were provided by Oxford university and one commercially available (Nanocyl NC 7000). Nanotubes were dispersed in aqueous surfactant solution with the aid of sonication and length (aspect ratio) was determined through SEM and TEM analysis. The average aspect ratio of MWCNTs was determined to be approximately 110, 210 and 225. MWCNTs were further dispersed into polyurethane latex and processed as nanocomposite by suspension casting. Electrical and mechanical properties of MWCNT/PU were measured. To the best of author's knowledge, this is first kind of study on morphology that employs latex technology as processing method. In the following texts, this part is referred to as "morphology study".

The second part of this study focuses on surfactant aspect of latex technology. It introduces a new surfactant Dabco DC 193 (DC193) which is known for its inertness [50] and compares its behaviour with TX100 and Sodium Dodecyl Sulfate (SDS). Both surfactants are commercially successful and known to be effective in producing CNTs dispersions. Sonication energy and its effects are also considered. The main aim of this part is to offer an efficient alternative to surfactants, that causes damage to environment. To the author's knowledge, it is first kind of detailed study which introduces a new surfactant and compares its long term stability with commercial surfactants. In this thesis, it has been reported for the first time that DC193 surfactant can be used to produce CNT dispersions which are stable in water for months. UV visible spectroscopy and Transmission electron microscopy is used to characterize the quality of dispersions. In the following texts, this part is referred to as "surfactant study".

Structurally, this thesis consists of a common introduction, literature review and experimental section to both of the studies. The chapter of experimental methods is subsequently followed by results and discussion, which is divided into two subchapters: one each for "morphology study" and "surfactant study". Each study has separate conclusion and finally, a general conclusion is presented with recommendation for further work.

2 Literature Review

This literature review consists of a brief introduction of CNTs and nanocomposites followed by section that thoroughly describes processing of nanocomposites, especially latex technology. A significant focus is kept on latex technology and related parameters because of its novel nature. It has been reported as an efficient, promising and simple method to prepare nanocomposites. Moreover, issues related to safety and commercialization of carbon nanotubes and CNT derived materials has also been addressed. Finally, this chapter is concluded with recent developments and future possibilities related to the field.

2.1 Nanotechnology and nanocomposites

Nanotechnology has been known for few decades now. The concept was first introduced in 1959 by professor Richard P. Feynman in his lecture: “There is plenty of room at the bottom” [51]. The term “nanotechnology” was coined by professor Norio Taniguchi in 1974. According to him “Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or one molecule” [52]. He used this term to refer to precisely manufacturing materials at nanometre level [51].

In a broad sense, nanotechnology refers to a group of techniques that operates on the scale of atoms and molecules. The word “nano” is used to represent measurements; a billionth of a meter is termed as “nanometre”. It has attracted attention in past few decades due to fact that materials property changes dramatically at nanoscale. These effects are called as “quantum effects”. Moreover, new properties emerge in materials with reduction in size, which are not exhibited by micro or macro scale [53]. For example carbon is soft in form of graphite: but at nanoscale it is stronger and much lighter than steel. Another example is zinc oxide, which is white on micro scale but becomes transparent at nanoscale.

Although the concept and terminology of nanomaterials is relatively new (around late 1980s), nanomaterials are have been used since the ancient era; Romans used nano sized metal particles to decorate their cups in 4^{th} century AD [54]. Other examples includes the use of coloured stained glass in middle ages, which were produced by reducing metal salts. Additionally, tyre industry is utilizing nano size reinforcements in the form of carbon black since 1912 [55]. A material can be classified as nanomaterial, if it has following key properties [56]:

- Dimensions (at least one) should be in the range of 1-100 nm.
- Processes involved in design must display fundamental control on attributes of molecular-scale structures (both physical and chemical).
- Larger structure can be prepared from them.

Nanotechnology is a vast topic which includes diverse fields such as medicine, biotechnology, energy storage, organic chemistry, semiconductors and many more. For the purpose of brevity, this literature review is focused on the nanocomposites only as they are the fundamental idea of this thesis.

2.2 Nanofillers

Fillers are the key ingredient of composites. Fillers are popularly used in micro form to improve the mechanical properties of binder (polymer matrix), which is inherently weak for some applications and requires strengthening. They are widely used in paper, coatings, adhesives, sealants, rubber and concrete too [57]. However, in the modern age of advanced materials, microfillers are slowly being replaced by nanofillers; as fillers are stepping out of their conventional role by imparting functional properties to materials. Currently, research is mainly focused on imparting superior electrical conductivity, barrier properties and fire resistance to materials. However, nanofillers are also known to improve other properties such as thermal and optical properties [58].

Nanofiller can be classified into the following categories: (i) One-dimensional nanofiller, (ii) Two-dimensional nanofiller, and (iii) Three-dimensional nanofiller (Figure 2.1.). Nanofillers, which are popular in nanocomposites includes nanoclays, nano oxides and carbon based nanofillers; which are explained very briefly in subsequent sections.

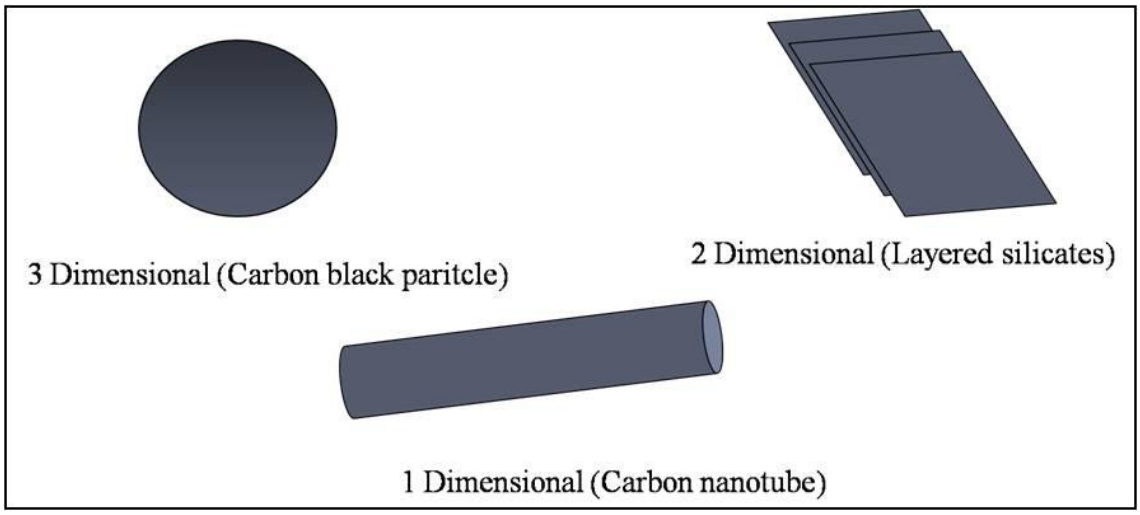


Figure 2.1 Classification of Nanofillers

2.2.1 Nanoclays

Nanoclays are abundant in nature and therefore, they are widely used as reinforcements for nanocomposites. They are classified on the basis of their crystal structure and sometimes on quantity and position of ions. The primary use of nanoclays is to strengthen the physical properties of polymers. Some of the popular clays available are phyllosilicates (smectites), organomodified montmorillonite (MMT), chlorite, centonite and many others. [58]

2.2.2 Nano-oxides

An oxide is compound that contains at least one atom of oxygen with other element. Most common nano-oxides that are used as fillers are titanium dioxide (anatase), alumina and antimony tin oxide in nano form. They are available as spherical particle with diameter around 15-20 nm [58]. However, Mogilevsky et al. reported that anatase can be altered into titanium nanotubes by hydrothermal synthesis [59].

Nanosilica is another oxide based material that is used as filler for nanocomposites. It is available in both natural and man-made form. Natural nanosilica, diatomite, is obtained from skeleton of diatomea; a unicellular algae which is formed in sedimentary layers. The average diameter of diatomite is 750 nm. On the other hand, synthetic nanosilica includes pyrogenic silica (5-100 nm) and fumed silica (100 nm) [58]. It has also been reported by Sha et al. that silicon nanotubes can be prepared using nanochannels such as Al_2O_3 using chemical vapour deposition (CVD) [60].

2.2.3 Carbon based nanofillers

Carbon based nanofillers have gained attention because they have ability to provide electrical conductivity to an insulating polymer matrix. Such conductive materials opens a possibility to replace expensive materials in the electronics industry [61], [62]. Carbon derived materials offer multiples advantage over conventional materials and are likely to substitute them. For example, CNTs are reported to be more efficient than the present materials (silicon) in transistors [62]. Another example is lead based solders, which are predicted to be replaced by CNT filled adhesives [63]. They also have shown potential to be used as reinforcing fillers; although, it has not been properly utilized yet [6]. This class of nanofillers mainly constitutes layered graphite, nanofibers and nanotubes. Layered graphite and nanofibers are described under next headings. However, detailed focus is given to CNTs in section 2.3 as they are the central idea of this thesis.

Layered graphite:

Graphite has been in use as conductive filler in polymer composites for few decades. However, it is slowly been replaced by nanofillers such as CNTs and graphene platelets

because conventional graphite is required in high amount (about 20% by weight) to form a conductive network. The primary reason behind this was the average particle size; which is in order few microns [64].

Vapour grown carbon nanofibers (VGCNFs):

VGCNF consist of similar graphitic structure as present in carbon nanotubes [53]. They are prepared by decomposing a hydrocarbon feedstock on metal catalyst. Generally, they have diameter around 50-200 nm and length about 100 µm. They are less popular than CNTs because of inferior mechanical properties (due to more micro-structural defects, higher density and large diameter). However, they have advantage of better availability and price, which is 50-60% less than for MWCNTs [65]. They might hold a key to replace nanotubes in some applications but an extensive research is required.

Graphene nanoplatelets (GNP):

GNP is a 2-dimensional nanofiller, which has been recently isolated and gained immediate attention from scientific community. It is a planar sp^2 bonded sheet of carbon with six membered carbon ring as unit cell. Figure 2.2 presents the basic crystal of graphene. It is also basic building block for CNTs, graphites and buckyballs [66]. Graphene is likely to give a stiff competition to CNTs due to its unique properties. It has exceptional electrical mobility and high mechanical stiffness. However, graphene based materials needs thorough research in order to make any commercial impact.

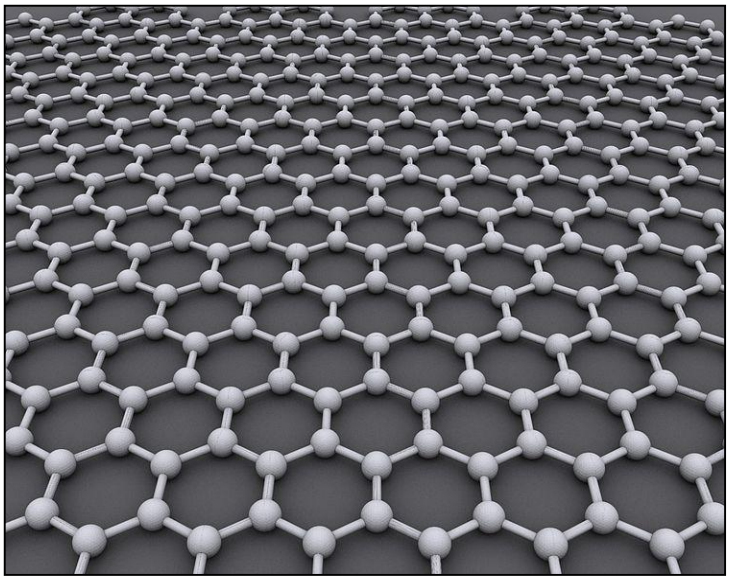


Figure 2.2 Structure of graphene crystal [67]

2.3 Carbon nanotubes

CNTs have gained exceptional popularity since their discovery. They are considered as the wonder material since their discovery in 1991 [68]. Their popularity among researchers can easily be estimated by number of publications per year as shown in Figure 2.3. According to the data collected through Scopus, more than 80,000 articles, conference papers and reviews have been published since 1990 [69].

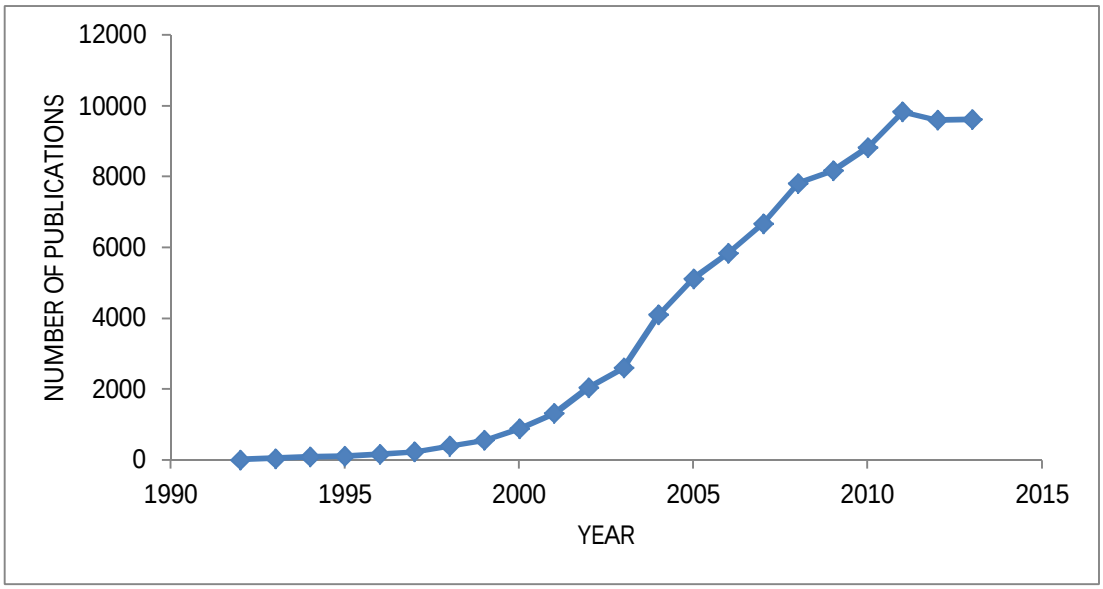


Figure 2.3 Number of publications related to carbon nanotubes

Structurally, CNTs belong to fullerene family of allotropes and can be visualized as a graphene sheet rolled into a cylinder [6]. Figure 2.4 presents the structure of single walled carbon nanotube (SWCNT). Popularity of CNTs can be attributed to their astonishing properties such as high tensile strength and modulus, thermal stability, excellent heat conductivity and electrical properties. Table 2.1 enlists experimental values of some properties of CNTs. CNTs have high elastic modulus of 1 TPa and tensile strength of 100 GPa, which is significantly higher than of any industrial fibre available [3]. Exceptional mechanical properties of CNTs can be credited to carbon-carbon bond which is the strongest in nature [2]. On the other hand, excellent electron transport properties are result of delocalized π-electrons along their walls [70]. CNTs can carry current up to 10^9 A/cm^2, which is three folds higher than copper wires [5]. CNTs also have excellent thermal conductivity of 6000 Watts/ (m K) [71].

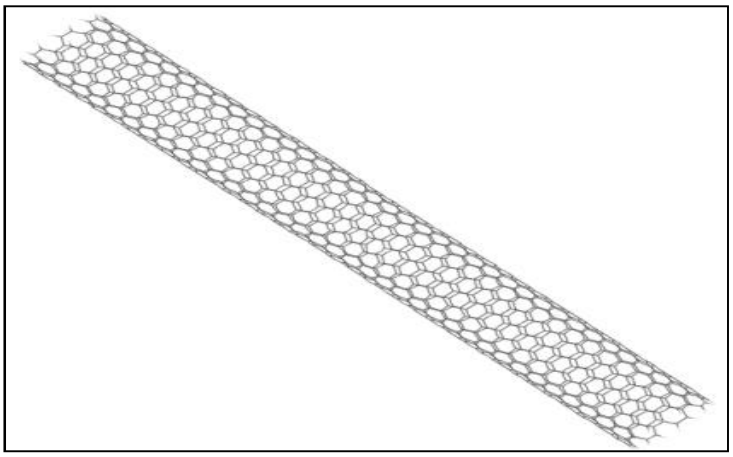


Figure 2.4 Molecular arrangement of carbon in carbon nanotubes [72]

Table 2.1 Properties of carbon nanotubes

Property	Value	References
Tensile strength	150-180 Gpa	[73] (as cited in [70])
Young's modulus	1-1.8 Tpa	[74][75](as cited in [56])
Heat conductivity	>6000 W/(m K)	[5]
Electrical Conductivity	10^9 A/cm^2	[5]

Moreover, CNTs also have high thermal stability; they are stable up to 2800 °C in vacuum and 750 °C in presence of oxygen [5]. However, it is worth mentioning that properties of carbon nanotubes are highly dependent on factors such as crystallinity, purity, number of walls and defect density.

2.3.1 Structure of CNTs

Each carbon atom in CNT is sp^2 hybridized and connected to three other neighbouring carbon atoms, which makes its structure similar to the one of graphite. CNTs are classified on the basis of concentric graphene sheets they contain. Single wall CNTs (SWCNT), double walled CNTs (DWCNT) and multi walled CNTs (MWCNT) are presented in the Figure 2.5.

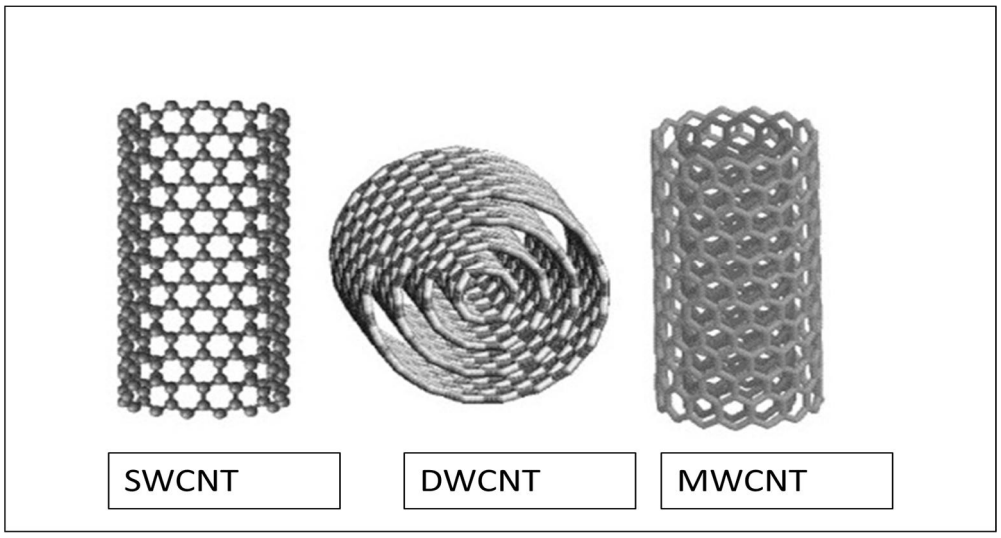


Figure 2.5 Classification of Nanotubes(Copyright [76]***, reprinted with permission from Elsevier)***

Another way to characterize the structure of CNTs is to analyze the manner of rolling in graphene sheet to form CNT. The rolling of graphene sheets into CNTs is defined by tube chirality (Equation 2.1) [71]. Chirality is defined by chiral vector (C_h) and chiral angle (θ).

$$C_h = ma_1 + na_2 \qquad \textit{Equation 2.1}$$

Where, (a_1,a_2) represents the unit vectors and (m, n) represents the number of steps along a_1 and a_2 in hexagonal lattice. Chiral angle determines the twist in the nanotube [71]. Figure 2.6 shows the possible conformations of rolling of graphene sheet into a CNT. It has been mentioned that chirality has a significant impact on electrical properties of carbon nanotubes [71]. CNTs are yet not a standard product, which means that characteristics like electrical conductivity, and mechanical properties strongly depend on manufacturing methods and its parameters. A change in conditions leads to change in structure characteristics (defects, crystallinity and chirality). Moreover, CNTs usually have defects in the form of pentagons and heptagons in their sidewalls. Such defects are also known to significantly affect the final properties of CNTs [3].

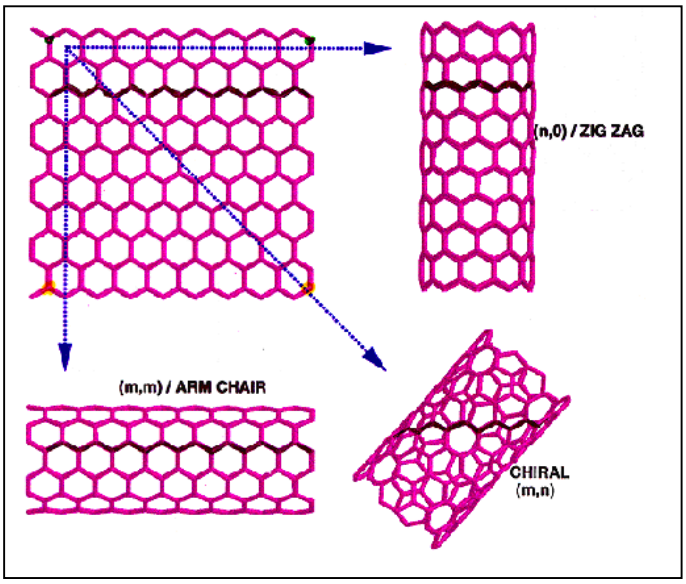


Figure 2.6 Rolling of graphite sheet to form carbon nanotubes [77]

2.3.2 Manufacturing of CNTs

Synthesis of CNTs has been improved significantly over the last decade [61], which was a result of extensive research and enthusiasm. Till date, few methods are available for synthesizing CNTs. Although, the methods have been improved over time, they still suffers from some major drawbacks such as low yield, high cost, presence of impurities and little control over morphology. Moreover, methods are usually sensitive to reaction parameters such as temperature, pressure and catalyst type [78]. Among the methods reported, the ones that have proved commercial significance are: chemical vapour deposition (CVD), laser ablation method, and arc discharge technique. Figure 2.7 presents the market share of produced CNTs by these methods. These methods are briefly described in following texts.

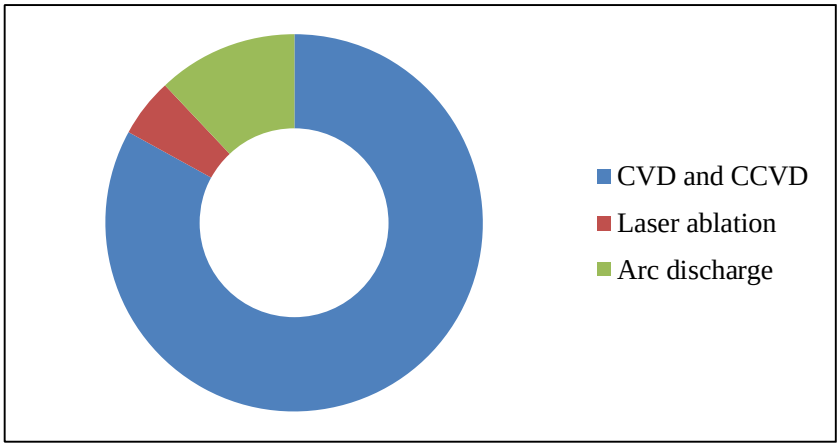


Figure 2.7 CNT market share on the basis of manufacturing technique in 2010 (adapted from [79] ***)***

Chemical vapour deposition (CVD):

CVD is the most popular method used for bulk production of CNTs. In this method, a mixture of hydrocarbon gases is decomposed on metallic particles such as Iron (Fe), Cobalt (Co) and Nickel (Ni). These particles behave as catalyst and nucleation site for the growth of CNTs. The temperature is kept between 500 -1000 °C and pressure at 1 atm. [80]. Fluidized bed reactors are used in this method, which provides uniform gas diffusion and heat transfer to metal catalyst. A common disadvantage of this method is that catalyst gets embedded in the nanotubes, which requires removal [15]. In spite of this drawback, CVD is most popular method for high volume production of CNTs.

Laser ablation method:

This method was reported for the first time by Smalley and his co-workers in 1993 [81] (as cited in [80]). A pulsed laser beam is used to vaporize carbon source, doped with metal catalyst such as Co and Ni. The reactor is filled with an inert gas (generally argon) at pressure of 0.7 atm., along with high temperature (around 1200 °C). Laser beam vaporizes the material and vaporized material condenses on other side of reactor. A major drawback of this method is that it consumes huge amount of electricity resulting from use of lasers, which leads to high costs; making it unsuitable for high volume commercial production.

Arc discharge technique:

Dr. Iijima [80] used this method to prepare CNTs, when they were accidentally discovered. A hot plasma discharge is created between two graphitic electrode separated by distance of 1 mm. Plasma formation is result of high voltage between electrodes (100 A; 20V). A complex mixture of products is produced when an atmosphere rich in He, N_2 and CH_4 is maintained [82].

Metal dusting:

This method is relatively recent and known for its impressive results. In this method, metal alloys are corroded and disintegrated in presence of strongly carburizing atmospheres, which produces a mixture of metal particles and carbon nanotubes. This method offers the following advantages: relatively moderate processing temperatures (650-750 ^{o}C), possibility of large volume production, low cost, and tailor ability of structure. However, it is worth mentioning that this method still requires detailed experiments and research work [78].

2.3.3 Commercialization of CNTs: a tough road ahead

Commercialization of any new technology needs persistence and patience. CNTs were discovered more than two decades ago and excitement still seems to be never ending. However, a pressure to commercialize has been building up for almost a decade now. CNT technology is facing a few challenges on their way to viable products. The major one being high risk factors in adapting to new technology, due to which material producer resist to invest in capital needed for scalability and quality improvement [61]. Nevertheless, CNTs have shown some promising advances. They are already been used for commercial products such as rechargeable batteries, sporting goods, automotive parts and water filters [3]. Arthur et al., in their review on commercialization of nanotubes, claim that things are optimistic for nanotubes and they will successfully commercialize in future [61].

Furthermore, the interest in this technology seems to be escalating with new potential applications emerging frequently [83]–[85]. Excitement, challenges and scepticism concerning graphene based nanomaterials are fittingly described in report entitled “How carbon cousins shaped warfare and can electrify the future” [86]. It has been mentioned that the challenge still to be faced is “to achieve high quality on a large scale and at low cost, and to interface and integrate the materials in devices.” According to Dr. Stephan Hoffmann, who is reader in nanotechnology in Department of Engineering at University of Cambridge “The field is at a very exciting stage. Now, not only can we ‘see’ and resolve their intricate structures, but new characterization techniques allow us to take real-time videos of how they assemble, atom by atom. We are beginning to understand what governs their growth and how they behave in industrially relevant environments. This allows us to better control their properties, alignment, location and interfaces with other materials, which is key to unlocking their commercial potential.” Andrea Ferrari, Director of the Cambridge Graphene Centre and doctoral training programme, describes the excitement related to carbon nanomaterials as beginning of a journey. The final outcome is unknown, but the potential of the materials encourages us to put a large effort early on.

It was observed that researchers are optimistic but often express their concerns. Recently, Bayer MaterialsScience, one of the leading manufacturers of CNTs, have closed their nano-project. According to Mr. Thomas, CEO of Bayer MaterialScience, "CNTs have a huge potential; however, applications for the mass market and chances of commercialization are not very promising in the near future" [87], [88]. Furthermore, emergence of graphene as potential substitute is also threatening for CNTs as they also have excellent properties. However, graphene is in its budding stage of development and it will be difficult to predict the scenario in next decade. Other barriers also exists such as the issue of quality, cost and toxicity. The issue of toxicity is discussed in detail in next section due to its direct influence on humans.

2.3.4 Toxicity and health hazards

CNTs are suspected carcinogens to mammalian cells and this issue is often less addressed in the research papers. Safe handling of CNTs is one of the major barrier that stands in their way of their commercial success. During literature review for this study, it was realized that knowledge about impact of CNTs on human health is not clear. Nevertheless, it is a common perception, which is aggravated by limited studies, that they can enter human body through skin or gut [89]. Koehler et al., in their review paper, also concludes that effect of CNTs has been poorly investigated and current impact assessment lacks proper research strategy [90].

The health effect of CNTs is determined by various factors such as type, surface characteristics, life cycle of product, end use, surrounding environment (chemical and physical) [90]. Dubey et al. concluded that "Kaajal" consists of CNTs, Kaajal is an ancient Indian eye cosmetic which is traditionally prepared by burning mustard oil in a lamp. The results of this study imply that there are some CNTs that are not hazardous to humans, in fact 'Kaajal' is known for treating common eye ailments. This property might be related to special structural property [91].

On the other hand, Lam et al. mentioned in their review paper that SWCNTs are even more harmful than quartz, which is considered as a serious health occupational hazard [92]. Additionally, Byrne and Baugh mentions that any particle having dimension less than 100 nm has unrestricted access to a significant area of lungs. Moreover, the nanoparticles have highest efficiency of deposition in lungs and can lead to chronic inflammation, epithelial injury, and pulmonary fibrosis. Eventually, they may lead to cancer in lung and abdomen lining [93]. Recently, a study supported to what they have predicted [94]. However, stable carbon nanotubes are now available, that maintain large agglomerates even when pressure of 100 kg/cm^2 is applied. They do not easily break into nanoparticles and hence, show low respirable dustiness. One of such kind of nanotubes is Baytubes®; according to manufacturer, no airborne baytubes were detected during production activities and compounding in air monitoring tests [95].

Taken together, there can be absolutely no doubt about the potential health hazards of CNTs; however, this field requires a detailed research strategy in order to determine the more accurate effects. The issue of health hazards needs to be resolved in order to streamline the use of CNTs in advanced materials. Safe handling of CNTs is critical for their success as the worker's safety at workplace needs to be assured.

2.3.5 Applications

Once the above mentioned drawbacks are surpassed; CNTs are likely to play an important role in numerous applications in various field such as nanocomposites, nanosensors, nano electronics, hydrogen storage and field emission devices [78]. It is believed

that nanocomposites are probably the first area where CNTs are having a commercial impact. In 2011, plastics and composites shared an 69% of global CNT market share with total sales of $475.9 million [79]. Figure 2.8 presents the market share of CNTs among popular applications in 2011. Several CNT filled materials are already available in the market such as racquets, surfboards, ice hockey sticks, golf clubs, transportation fuel system components, plastic additives, battery electrode additives [3], [79].

On the other hand, CNTs in nanoelectronics are also widely researched currently and have shown prominent advances [61], [62]. It has been predicted that by the year 2016, CNTs will make biggest advances in electronics and data storage market [79]. However, this literature review mainly focuses on nanocomposites, as they are the central idea of the thesis.

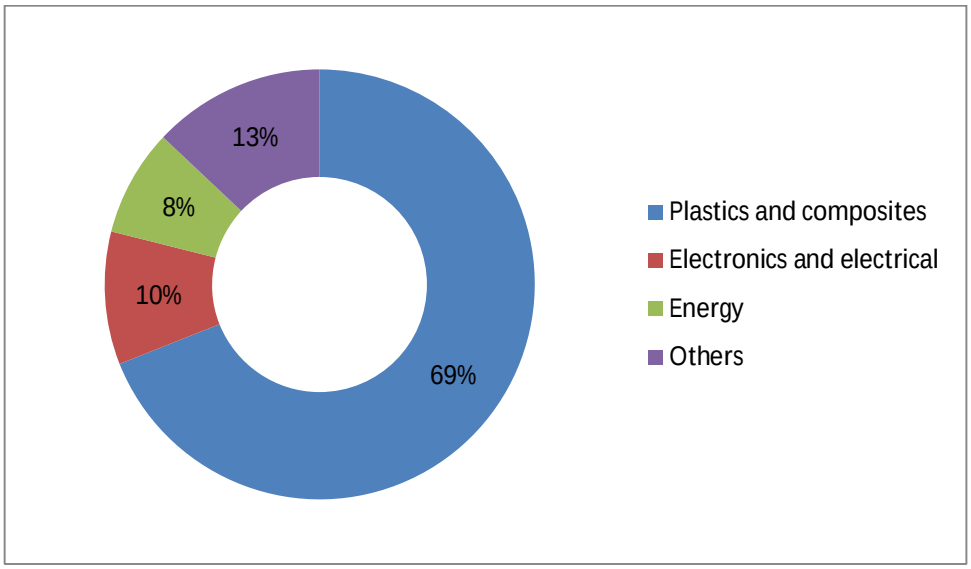


Figure 2.8 CNT market analysis by industry (2011) (adapted from [79]***)***

2.3.6 Recent developments and future trends of CNTs

In the recent years, GNPs are seen as a big contender among nanofillers. Carbon nanotubes are likely to face strong competition from them. Mittal et al., in their review, stressed that GNPs are more advantageous than CNTs as they imparts improved mechanical properties due to better load transfer, which can be attributed to their planar structure and high aspect ratio [80]. Moreover, GNPs are less toxic, which makes them easy to handle as compared to CNTs [96]. However, GNP technology is in budding state of technological development; therefore, it is difficult to predict the situation in couple of decades from now. Although, development of GNP technology has certain advantages over CNT technology; as successes and failures from extensive research of nanotubes are likely to serve as valuable lessons for developing graphene based materials [61]. Therefore, they might take less time to commercialize than expected.

Meanwhile, CNTs are continuously undermining our knowledge about behaviour of nanomaterials. An interesting finding was reported by Ozden and co-workers. They shot MWCNTs towards an aluminium target at the speed of approximately 24000 Km/hr. It was expected and wrongfully predicted by simulations that CNTs will break into pieces when large force is applied on them. Actually, it was found that when struck at incident angle of 90º (head-on), CNTs were deformed drastically. On the other hand, a parallel impact results in unzipping of nanotube to form a graphene nanoribbon. [97]

Another study proposes an argument that the structure of CNTs is different from the one that was earlier predicted and popularly believed by scientific community. Conventionally CNTs are reported as graphene cylinders; however, Lee et al., in their research, concluded that CNTs are graphene helix. They also believe that this might be true for all the CNTs. Dr. Lee states that "The outcome of our study is likely to create a stir in the academic circles of physics and nano-materials, since it will be necessary to modify numerous research findings that have been done over the past 20 years." [98]. Such studies signify that still carbon nanotubes are able to surprise us even after two decades of extensive research. Nevertheless, the CNT technology is slowly and steadily advancing ahead. Commercial giants have also started embracing CNT technology. IBM, for example, has shown intentions to replace silicon transistors with CNT based transistors by 2020. Transistors based on carbon nanotubes are expected to be 5 times faster than most efficient silicon transistor. [62]

2.4 Polymeric nanocomposites

Human history is conventionally classified on the basis of how we have interacted with materials. This is a convenient convention because our ancestors usually left materials as the only permanent records of their existence. These eras are termed as Stone age, Bronze age and Iron age. If this convention is still followed, the modern age will be termed as polymer age [99]. Polymers are known to us since a long time. However, first synthetic polymers were derived from natural polymers such as nitrated cellulose in the 19^{th} century. Although, the polymer chemistry was not understood at that time; Bakelite was already available in commercial market in the beginning of 1900s. At that time, polymers were still believed to be an aggregate of small molecules joined by mysterious secondary forces [99].

The first significant advances in polymer science were reported by German chemist Hermann Staudinger, when he published his theory on macromolecular hypotheses in 1933 (and coined the term macromolecules). He explained that astonishing properties of polymers are attributed to intermolecular forces between molecules of large molecular weight [100] (as cited in [99]). In the next decade, the extensive work by prominent scientists such as Wallace H. Carothers, Karl Ziegler and Paul Flory laid the foundation of polymer science and engineering [99].

Since then, polymers have stepped up into almost all segments of applications. Polymers are key materials in wide range of products like milk bottles to bulletproof vests. In 1950s, polymer industry observed a major shift towards novel materials with enhanced properties [101]. In earlier days, main focus was on search for new monomers. With advances in polymer technology, efforts were directed towards improving properties by blending available plastics. However, as the time progressed - high stiffness and improved strength was needed for engineering applications and blending of polymers was not enough to provide such ultimate properties. These requirements were generally fulfilled by processing polymeric materials in following ways [101]: creating unidirectional structures with aligned polymeric chains and forming composite materials with fillers and fibres of high aspect ratio.

After a while, the demand for functional plastics was observed, the focus shifted on nanocomposites as they have significantly enhanced properties at very low filler content. Since the discovery of CNTs, they are considered as the next best thing for polymeric composites. CNTs can impart wide range of functional properties to nanocomposites. It is worth mentioning that processing of CNT filled polymeric composites on a large scale is still a challenge. Generally, repeatability of results and effectiveness of methods in properly dispersing the CNTs is mentioned with concern [102]–[107]. In the last decade, considerable research has been focused on using environment friendly methods such as latex technology, which uses water as a dispersing medium [9], [70], [108]–[117]. Manufacturing of CNT filled nanocomposites is explained in more detail in Section 2.5.

2.4.1 Properties of CNT filled nanocomposites

CNTs are reported to be an ideal filler for nanocomposites. In fact, polymeric nanocomposites are one of the major applications of carbon nanotubes. CNTs can be used as conductive and reinforcing fillers in polymeric matrices. The materials formed in this manner can be employed in various sectors such as sports industry [80], aerospace and electronics [70]. In electronics, the basic idea is to replace metals and semiconductors with cheaper conductive plastic.

Polymer matrix are usually insulating in nature; however, modern applications such as static dissipative materials, conductive inks and many more require a considerable amount of conductivity in the plastic. Conductive fillers are excellent means to decrease the overall resistivity of materials by many orders. However, in order to do so; they are required to form a conductive 3 dimensional network throughout a matrix. The transit of material from an insulating to conductive one is termed as percolation and the concentration of filler at which such behaviour is observed is termed as percolation threshold [118]. In composites based on conductive fillers, percolation theory is regularly used to explain the insulator to conductor changeover [119]. The theory of percolation can be

explained in simpler words in a following manner: when filler is present in amount less than percolation threshold, it exists as individual particle or cluster and electrical conductivity of the composite is still close to pure polymer. However, when the quantity of filler is increased to a critical value, a 3D network is formed and conductivity is radically increased [70]. Percolation threshold is affected by many factors such as polymer type, CNT type, crystallinity, viscosity, dispersion method, treatment method and many more. However, morphology and aspect ratio of filler is considered most critical parameter in determining the electrical properties of CNTs. According to popular theory [9], The volume fraction (φ_c) needed for creating a percolation network is inversely proportional to aspect ratio of CNTs.

Percolation threshold is one of the most widely researched topic in CNT filled nanocomposites. A total number of 895 papers have been published until now related to percolation in CNT filled nanocomposites [120]. A percolation threshold between 0.05 and 10 wt% for CNTs have been reported from various experiments by the researchers [118], [119]. Figure 2.9 presents the number of publications with various CNT-polymer systems along with minimum percolation threshold reported. This huge difference in the value can be attributed to different type of CNTs and different processing methods used by researchers. Ideally, if CNTs are not well dispersed they will behave as microfillers and conductive network will be formed at high concentration resulting in higher percolation threshold. Depending on the mobility of filler particles, percolation threshold can be classified into category: statistical percolation threshold and kinetic percolation threshold. The major difference between the two is that in kinetic percolation threshold particles are free to move and thus forming a conductive network at less concentration than statistical percolation threshold is achieved [118].

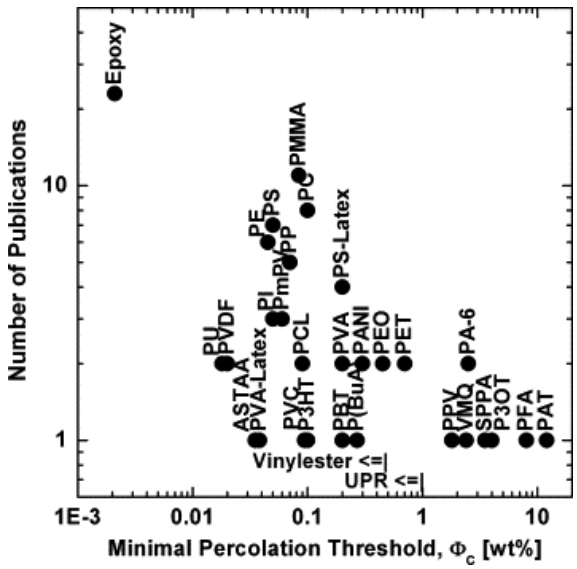


Figure 2.9 Minimal percolation threshold v/s number of publications for polymer systems(copyright [21]***, reprinted with permission from Elsevier)***

Apart from electrical properties, CNTs have also shown potential as reinforcing filler. CNTs, if properly dispersed, are able to generate large amount of interfaces which are primarily responsible for exceptional and unique properties of nanocomposites. The interface to volume ratio is substantially higher as compared to conventional composites; which allows to reduce the volume fraction of reinforced phase without degrading the other properties of polymers [78]. CNTs have outstanding modulus and tensile strength, which is attributed to their structure consisting of carbon-carbon covalent bond. This bond is strongest in nature and responsible for the extreme strength of diamond. Therefore, CNTs are suitable candidate for reinforcing polymers. In the last decade, much of research has been focused on enhancing mechanical properties of polymers with the help of CNTs [78]. Researchers have reported excellent results but such occurrences are rare. A vast disagreement exists between theoretical and experimental value especially for thermoplastic nanocomposites [6]. The main reasons for this diminished mechanical properties of nanocomposites are:

- Individual dispersion of CNTs is unrealistic, some amount of agglomeration eventually happens due to high magnitude of vdw forces.
- Reduction in aspect ratio during processing.
- Increase in defect density during functionalization.
- Weak interfacial bonding between CNTs and polymers.

The main requirement of a processing method is to achieve the fine dispersion of nanofillers. Apart from that, interfacial bonding between nanotubes and polymeric chains is also very critical. Weak interfacial bonding causes polymeric chains to slip under external force, leading to decreased load carrying capacity [78]. It can also result in yielding, as weakly bonded nanoparticles can act as voids leading to cavitations. This leads to strain softening and large strains to failure [78]. Moreover, glass transition temperature (Tg) is also dependant on quality of interface. It can increase or decrease depending on the magnitude of interfacial bonding.

Apart from strengthening of polymers, CNTs also improve the fracture toughness of polymers. It is well known fact that composites fracture due to formation of microcracks, which propagates rapidly under load. In case of CNT filled nanocomposites, when a crack reaches CNT- it cannot propagate through CNT due presence of graphene layers (which contains C-C bonds; strongest bond in nature). Hence, the crack has to pass along CNT and consumes more energy. Thus it results in increase of fracture toughness [28]. Nevertheless, the potential of CNTs as reinforcing nanofillers cannot be denied, but it can be agreed that the true potential has not been reached yet [121]. On the basis of cost-property analysis, that future of CNTs as reinforcing nanofillers is not very promising [6].

CNTs are also known to impart superior thermal conductivity to the nano composites. For the purpose of brevity, this application and its significance is not mentioned in this literature review. However, it is worth mentioning that this application have big potential as adding 1 volume % of CNTs can increase the thermal conductivity of base polymer by 100% [122]. Such impressive results make them viable candidates to replace metals in power electronics, heat exchangers and many more applications [123].

2.4.2 Parameters affecting the properties of nanocomposites

The processes employed for preparing nanocomposites are very delicate in nature and a detailed knowhow is required in order to ensure the repeatability of results and prediction of end properties. Following parameters are known to affect the performance properties (electrical, mechanical and thermal) of CNT filled nanocomposites [118]:

- Entanglement state of CNTs.
- Preparing method of CNTs.
- Functionalization method.
- Dimensionality.
- Dispersion method.
- Polymer type.
- Composite processing method.
- CNT morphology.
- Interfacial bonding.

Although the list is extensive and processing options are many, choosing parameters for experiments usually depends on availability of resources, bottle necks, timeline for development and experience. All the parameters considered together: the primary aim of the process is to achieve finely dispersed CNTs with strong interfacial bonding to polymer matrix. It is worth mentioning that Boa et al. presented a model in which they proposed that dispersion state is most important parameter that affects the property of CNTs [24].

2.4.3 Aspect ratio, length or diameter: what matters the most?

Since this study attempts to evaluate the effect of CNT morphology on electrical and mechanical properties of nanocomposites. It is worth mentioning that, till now, aspect ratio is considered to be more critical parameter in determining the PT in nanocomposites [23]–[28], [118]. It has been statistically calculated that for aspect ratio of 1000 the PT will be around 0.1% given that the CNTs are finely dispersed in nanocomposites [124] (as cited in [118]). Moreover, it has been predicted that PT changes up to three orders of magnitude when aspect ratio is varied from 10 to 10000 [24]. However, other factor such as length and diameter are rarely considered as influencing factors. Calcula-

tions on the basis of aspect ratio could be misleading as it is a relative quantity. For example, to obtain aspect ratio of 100 - the dimensions of CNTs can be 1000 nm as length and 10 nm as diameter or 5 µm of length and 50 nm as diameter. Both nanotubes are likely to behave differently in nanocomposites. Furthermore, thinner nanotubes are likely to bend more due to thermal stresses developed during processing and cooling of matrix as they have lower bending stiffness [28]. The effect of CNT morphology and its implications are discussed in detail in results and discussion section of this thesis.

2.4.4 Applications of CNT filled polymeric composites

The variety of properties exhibit by CNT filled nanocomposites have made them relevant for multiple applications. Table 2.2 enlists various popular applications on the basis of exhibited property.

Table 2.2 Most common applications of CNTs along with relevant property [125]

Relevant property	**Application**
Electrical properties	Conductive plastics for electrostatic dissipation and shielding, Conductive sealants; charge storage for super capacitors and fuel cells; conductive inks and adhesives
Mechanical properties	Wear resistant coating, high performance fibers and coatings
Thermal properties	Thermal conductive composites and paints
Field emission properties	Flat panel displays and electron device cathodes

2.5 Preparation of CNT filled polymeric nanocomposites

One of the biggest challenges in CNT technology is preparing finely dispersed nanocomposites. As mentioned before, CNTs are available as highly entangled bundles, which are thermodynamically stabilized by π-π interactions [70]. Vdw forces also contributes to this tube-tube attraction, with magnitude as high as 500 eV/µm [18]. Due to this large magnitude of attraction, CNTs have tendency to remain bundled, even when attempted to disperse through external aid like sonication. Baughman et al. have reported that presence these bundles results in reduced mechanical and electrical properties [126] (as cited in [70]). Hence, CNTs should be finely dispersed in polymers. Some of the challenges that has often been encountered while processing are mentioned in section 2.4.1.

Various methods have been reported for preparing CNT filled nanocomposites. The most common ones are: solution processing, in-situ polymerization, melt processing, extrusion and bulk mixing [9]. Other methods have also been reported such as coagulation spinning, mechano-chemical pulverization, solid-state shear pulverization, electro spinning [6]. However, this literature review discusses and compares the most widely used methods: melt processing, in-situ polymerization and solution processing.

These all methods consists of different processing routes but they all refer to common issues like exfoliation of CNT bundles, homogeneous dispersion in matrix and interfacial bonding [127]. The properties of nanocomposites (electrical and mechanical) are highly dependent on choice of processing method [128]. As expected, this is due to fact that different methods produces different quality of dispersion and alignment of carbon nanotubes in matrix. Figure 2.10 presents the contrast in various processing methods commonly used to prepare CNT filled nanocomposites. A large volume of literature is available on these processing methods [6], [19]. However, here they are compared just briefly in order to stress why a particular method is selected for this study.

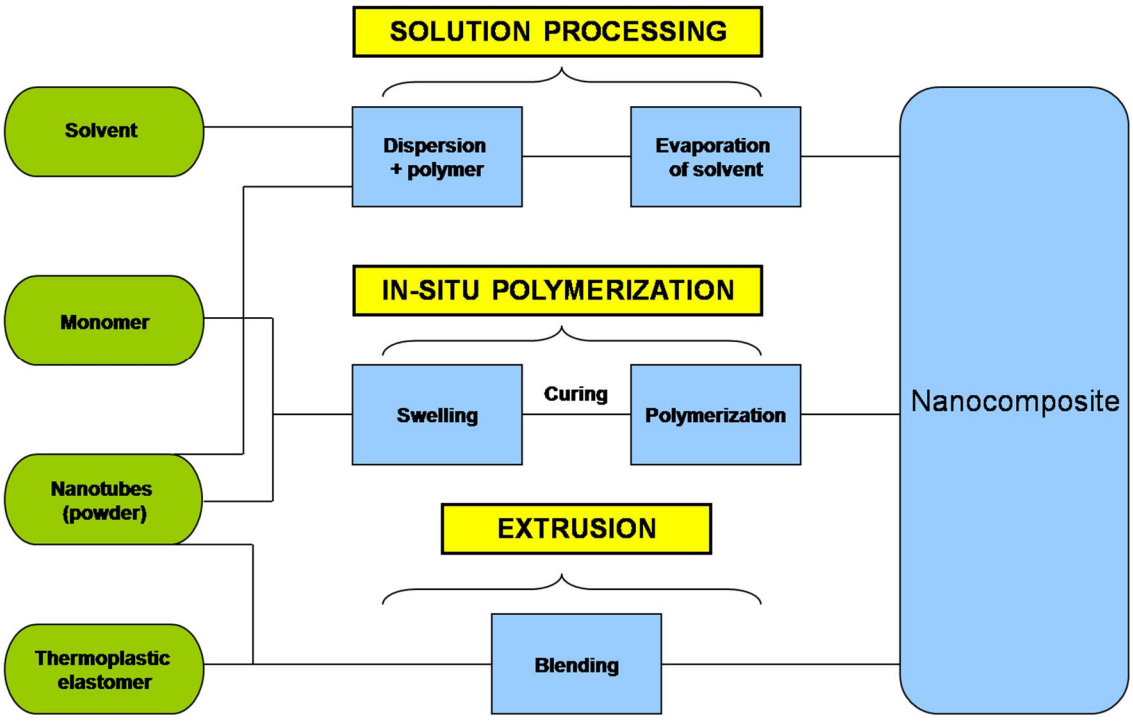


Figure 2.10 Flowchart depicting popular processing methods for preparing of CNT filled nanocomposites

Melt processing:

This method is generally used for thermoplastic polymers such as polypropylene and polycarbonate. CNTs are blended in melted polymer to form a viscous liquid, which solidifies on cooling to form a nanocomposite. Quality of dispersion is enhanced by

shear mixing through extrusion and injection moulding. The parameters that affects quality of dispersion includes screw speed, melt temperature, residence time and screw configuration [6]. This method can be considered as most compatible method with industrial practices that are currently available. However, this method is not as effective as solution processing due to high viscosity of thermoplastics, which act as barrier in uniformly distributing CNTs in matrix [80]. Moreover, composites only with low filler concentrations can be processed by this method [19].

In situ polymerization:

This method is known for its efficiency in producing uniformly dispersed nanocomposites. It involves mixing CNTs with monomers and polymerizing them via addition or condensation polymerization. Sonication is usually used to disperse nanotubes. A major advantage of this method is that polymerization is held around exfoliated CNTs; a polymer mass is created them which prohibits re-agglomeration. Additionally, a covalent bond can be formed between CNTs and polymer matrix that leads to improved mechanical properties due to enhanced interfacial bonding. [19]

Solution Processing:

This is the most common method used for preparing CNT filled nanocomposites. A common solvent is used to mix both components (CNTs and polymer) and later solvent is evaporated to form a composite film. Vigorous stirring or sonication is generally employed in this method [127]. However, vigorous stirring alone is not usually adequate for creating proper dispersion of CNTs [70]. This method is known for producing excellent results with thermosetting and thermoplastic resins [11], [12], [70], [129]. An important challenge is to disperse CNT powder in a solvent, and more important is to find a suitable solvent. Dispersion states of carbon nanotubes in a solvent is a complicated phenomenon, which is affected by two simultaneously opposing interactions: (i) interaction among CNT threads, and (ii) interaction between CNT threads and dispersion medium (solvent) [15].

Ham et al. reports that Hansen solubility parameters (HSPs) can be used in predicting the suitability of solvent for dispersing CNTs. HSPs are basically scientific explanation behind the famous quote of chemistry "like dissolves like". They predict if two different types of molecules will be compatible with each other or not. HSPs are already used to explain the miscibility of polymers and solvents, and organoclays in organic solvents. HSP are explained by the equation: $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, where δ_d is energy from dispersion forces between molecules, δ_p is energy from polar forces and δ_h energy from hydrogen bonding between molecules. It was concluded that dispersion state of CNTs depends on the dispersion component (δ_d) of HSPs. Furthermore, nanotubes precipitates in solvents with high δ_p and δ_h (such as water). They divided solvents into three

categories depending on the state of CNTs in dispersion they produce: dispersed, swollen and sedimented. Among 19 common solvents, only DMF, Chloroform and NMP are reported to constitute dispersed category and are able to prepare stable dispersion without any external aid. Water was reported in sedimented category [15].

2.6 Latex Technology

Latex technology is a unique offshoot of solution processing which have recently emerged as efficient method to prepare CNT filled nanocomposites; instead of using solution of polymer in organic solvents - it benefits from polymer latexes. Latexes are stable suspensions of tiny polymer particles suspended in water. The size of particles is generally few hundred nanometres in diameter. In this process, CNTs are dispersed in water with aid of surfactant and blended with latex; which is later casted on a mould to get a polymer film. It can also be freeze dried and injection moulded to get bulk polymer [70].

This technology is rather new, which has recently gained much interest due to its environment friendly nature. Till date, only 42 research articles are available [130]. It has been proved that this technology has potential in successful commercialization especially by Grossiord and co-workers [70], [108]–[112]. Moreover, many studies have been published in the recent years that has provided convincing results and proven the potential of this technology [9], [113]–[117]. Using water as dispersion medium instead of organic solvents offer following advantages: (i). organic solvents may lead to adverse health effects, (ii). water is universally available and can be easily obtained in ultrapure form, (iii). carbon nanotubes dispersed using water can be employed in fields such as biochemistry and biomedical engineering, where organic solvents cannot be used for their evident incompatibility [131]. Moreover, it has comparably less evaporation rate at high temperatures with respect to organic solvents. This is certainly an advantage because there can be swift rise in temperature during sonication causing damage to organic molecules of surfactants.

As mentioned before, CNTs are inherently hydrophobic in nature; hence, they spontaneously agglomerate when tried to disperse in water by sonication [132]. However, if CNTs are surface modified, they are capable of producing a stable dispersion in water. Surface modification can be done by both covalent and non-covalent methods [18]. Covalent methods include functionalization through various chemical treatments such as acid chloride condensation [15], fluorination [70]. These methods modify the surface of CNTs resulting in change in surface properties. Such methods usually involves oxidizing CNTs with acids, which creates defects in CNT walls (change in π electron cloud) and induce shortening of length resulting in diminished electrical and mechanical properties [8], [18]. Moreover, such methods leads to increase in capital investment and thus making them commercially undesirable [6].

Such damage to the CNTs can be prevented by using non covalent functionalization methods. These methods generally use using a third component termed as surfactant [70]. Surfactants are chemical moieties that gets absorbed on the CNT surface either by π-π interactions or coulomb attraction during sonication [18]. The colloidal stability of suspended CNTs can be explained by electrostatic and/or steric repulsion among functionalized CNTs [70]. Some of the common surfactants used for dispersion are sodium dodecyl benzenesulfonate (SDBS), octyl phenol ethoxylate (TX100), sodium dodecyl sulfate (SDS), dodecyltrimethyl - ammoniumbromide (DTAB), and hexadecyltrimethyl - ammoniumbromide (CTAB) [18]. Non covalent method is considered superior as it causes no change in π-electron cloud of graphene layers, and thus causing no harm to electrical and thermal properties of nanotubes [18]. Moreover, CNTs dispersed using surfactants are known to be more compatible with living organisms [133]. This thesis deals with using surfactants for creating a stable dispersion of carbon nanotubes, therefore it is discussed in detail in section 2.6.1.

A stable dispersion of CNTs in water is necessary for preparing finely dispersed nanocomposites. However, due to complicated surface chemistry between CNTs and surfactants – it requires thorough experiments and systematic research. A number of factors need to be considered for fine dispersion of CNTs in matrix. Various factors known to influence the quality of CNT dispersion in water are:

- Type of surfactant [18].
- Surfactant concentration [18].
- Time of sonication [8].
- Sonicating power or energy [8].
- Purity of CNTs [70].
- Pre-treatment of CNTs [19].
- Type of sonication equipment (bath sonicator/tip sonicator[112], [134].
- Defect density on surface of nanotubes [135].
- Structure of entangled network and density of CNT [136].

Latex film formation is now a well understood phenomenon. It can be utilized for developing novel coatings and adhesives. It has been reported that by careful control of drying conditions and two phase particles, the structure of material can be controlled to tens of nanometres. Additionally, blending of nanoparticles with latexes allows a simplistic approach to ensure fine dispersion [9]. Moreover, this method results in improved thermal conductivity of nanocomposites. However, it has also been reported that weight ratio of surfactant to CNT must be optimized in order to obtain maximum thermal conductivity [114].

2.6.1 Use of Surfactants

A fine dispersion of CNTs in liquid phase can be achieved by two methods: first one is if free energy change in mixing is negative ($\Delta G_{mix} < 0$), another one involves using of surfactant as dispersion aid. However, the free energy of mixing can only be minimized when the concentration of SWCNT is less than 20 µgm ml^{-1} [137]. It has been reported that surfactants are able to modify the particle-medium interface and prevent them from aggregating [138] (as cited in [139]) . In their report, Fagan et al. simply elaborated the physical mechanism that prevents agglomeration of CNTs in surfactant assisted systems [137]. Surfactant molecules, completely or partially, covers the separated nanotubes and thus preventing them from re-agglomerating by acting as barrier to vdw forces. Three principles by which surfactants leads to stable suspension of carbon nanotubes in water: electrostatic repulsion between the particles, steric hindrance caused by absorbed layer and reduction of hydrophobic linkages among particles [139]. If the concentration of surfactants in medium is lowered, molecules of surfactants will leave the CNTs causing them to agglomerate. Therefore, surfactants are required to be present in sufficient amount. On the other hand, larger molecules such as DNA or polymers the mechanism believed to be different as desorption of such large molecules is unlikely [137].

Surfactants can be divided into two categories: ionic and non-ionic surfactant and both type are widely used in preparing CNT dispersions in liquid mediums. Few popular ionic surfactants that are known for producing stable suspension are SDS, SDBS and CTAB. On the other hand, efficient non-ionic surfactant includes TX100, Tween 80, Tween 20, Triton X 405 [39], [49]. Few studies are available that compare the efficiency of various surfactants. Nikolosi et al. (as cited in [140]) reports the order of various ionic surfactants in the following order: SDS>LDS>SDBS>TTAB>SC. On the other hand, Rastogi et al. reported that TX100 is most efficient surfactant among SDS, Tween 20, Tween 80 and TX100. They reported order of effectiveness on the basis of dispersion power as TX100 > Tween 80> Tween 20>SDS [18]. It has been reported that efficiency of surfactant depends on characteristics of CNTs [39]. For example, the higher number of walls will lead to heavier CNTs and therefore, they will have higher tendency to settle down when dispersed.

In the presence of sonication, nanotubes separates from the bundle by a process called “unzipping”. These separated nanotubes are surrounded by surfactant molecules present in medium, which wraps around the nanotubes and prevent them from forming re-agglomerates. Strano et al. reports the mechanism of this unzipping. They claim that sonication creates gaps at the end of bundle. Surfactants are adsorbed in these gaps and CNTs separates from bundle along its length. Finally, a secluded CNT is released and suspended in the dispersion. They also reported that all the nanotubes are not individualized in surfactant solution. Individual CNTs are likely to form a dynamic equilibrium with small agglomerates [141]. In order to understand the role of surfactants in stable

CNT dispersions, their arrangement on CNT surface should also be considered. There are few studies available that study arrangement of surfactant molecules on surface of nanotubes. According to Ji et al., surfactants form a monolayer, with molecules resting with vertical alignment of the tail on surface [131].

According to Vaisman et al., ionic surfactants are favoured for CNT-water suspension and non-ionic for organic solvents. They also mentioned that a conclusion cannot be made that anionic surfactants are better than cationic surfactants in dispersing the CNTs [142]. Literature review during this thesis also supported this claim. There is considerable amount of literature where non-ionic surfactants are successfully employed for producing stable dispersion of CNTs in water [18], [39], [143], [144]. Additionally, Rastogi et al. reported that TX100 (non-ionic surfactant) has better dispersing power than SDS (ionic in nature) for dispersing CNTs in water [18].

Concerning surfactants, various factors are known to play decisive role in stability of suspension which are: nature of surfactant, concentration and type of interaction [142]. Moreover, surface charge of CNTs after dispersion also plays an important role. Jiang et al. has proved that carbon nanotubes act as negatively charged particles in water through zeta-potential analysis[139]. However, Matarredona et al. demonstrates that carbon nanotubes can attain negative or positive charge depending on pH of the dispersing media [131]. Furthermore, the magnitude of this charge is controlled by purification process and wall functionalization of CNTs. For ionic surfactants, stability of suspension depends on absorbing mechanism, which is supported by electrostatic interaction with the surface of nanotubes. Hence, many factors in a particular CNT surfactant pair needs to be considered in order to determine the effectiveness of surfactant. If chemical structure of surfactants is considered, following chemical groups are known to enhance the effectiveness of the surfactant: (i) benzene rings [145] and (ii) double bonds [146]. It is worth mentioning that surfactants are also technique specific; which means that a particular surfactant can be effective for one technique but behave differently for other technique [39].

Taken together, surfactants are most critical component in a stable CNT-surfactant-water system. However, it should be kept in mind that there are far too many parameters that needs to be considered before selecting a surfactant. Moreover, test trials are required to verify their efficiency for a particular CNT and optimize the concentration for maximum stability [18].

2.6.2 Effects of surfactant on properties of nanocomposites

It has been proven that surfactants play most critical role in dispersing nanotubes in nanocomposites prepared by latex technology. However, they have a disadvantage that surfactants get trapped at interfaces between nanotubes and matrix. Therefore, they alter

the properties of nanocomposites. One example of this occurrence is decrease in thermal conductivity due to phonon scattering [147]. Additionally, It has been reported that surfactants acts as plasticizers leading to diminished mechanical properties [148]–[150].

2.6.3 Dispersion of CNTs in water: use of ultrasonic energy

Exfoliation is the term given to separating of CNTs from agglomerates; the task is difficult - given the high magnitude of interactional forces between the two CNTs. Commercially supplied CNTs are in the form of aggregated bundles [8]. Efforts have been made to develop various techniques to disperse the CNTs. Most popular techniques consists of sonication, calendaring, ball milling, shear mixing and extrusion [8][19]. Characteristics of these methods are listed in Table 2.3, which is provided as a guideline for selecting an appropriate method used in this thesis. Sonication is an effective tool for dispersing CNT in liquid medium; it has been extensively studied by researchers and reported to be an successful approach [8], [111], [112], [151]. Sonication is required as external aid because even with the presence of surfactant the free energy of mixing ΔG_{mix} for individualization of nanotubes is positive and hence not spontaneous in nature [137].

Table 2.3 Characteristics of dispersion techniques for dispersion of carbon nanotubes in polymer matrix (adapted and modified from [19] ***)***

	Damage to CNTs	**Parameters**	**Advantages**	**Disadvantages**
Sonication	Yes	Sonication power, volume of liquid, frequency, shape of vessel	Easy to use, reproducible results	Heat generation, noise pollution
Calendaring	No	Rotation speed, distance between rolls	CNTs may be aligned to matrix	Operation training. Difficult to clean
Ball milling	Yes	Diameter of mill, radius of balls, volume of polymer, volume of balls, material of balls and many others	Easy to operate, widely used for coatings	Difficult to clean, takes long time for dispersion
Shear mixing	No	Size and shape of blade, viscosity of mixture, mixing speed, time	Easy to clean after use	Less effective
Extrusion	Yes	Geometry of screw, rotation speed, length of screw, temperature profile	Large scale production	Less effective

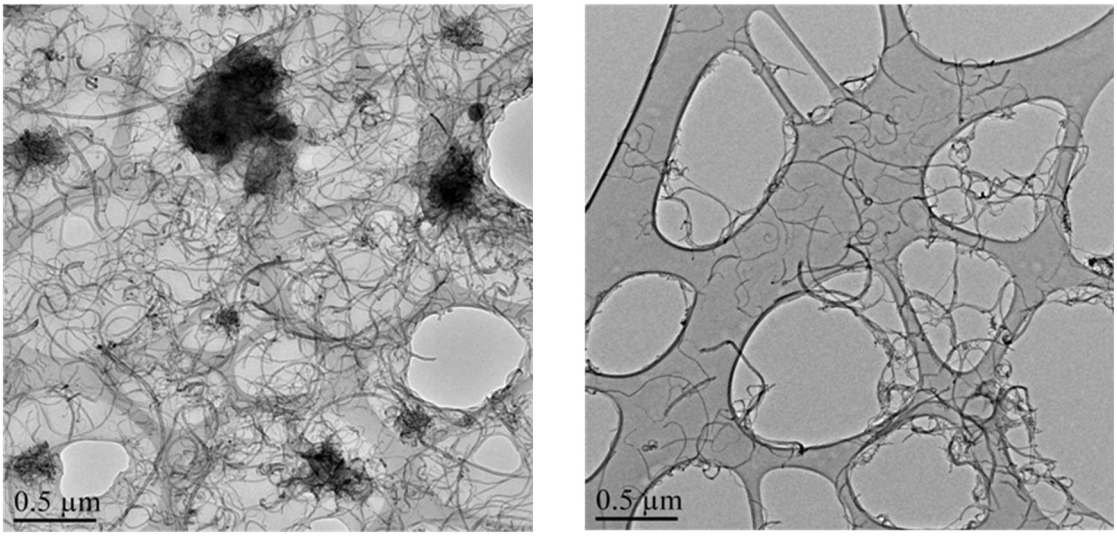
It has been reported that sonication energy, not the sonication time is more precise parameter in determining the optimum dispersion state of carbon nanotubes [8], [112]. The following equation defines the sonication energy (E):

$$E = P * t/V \qquad \textbf{\textit{Equation 2.2}}$$

Where P is output power in watts, t is time of sonication in seconds, and V is total volume of liquid in millilitres. This topic has been extensively researched by Gossiord and co-workers. According to them, characterizing the dispersion state with sonication energy provides reproducible results [44], [70]. During sonication, ultrasound waves induce a series of rarefaction and compression in the molecules of medium; the molecules of liquid start vibrating around their mean position. At certain amplitude, the rarefaction is sufficient to overcome the cohesive forces of the molecules-which generate cavitation bubbles. These bubbles grow to a particular equilibrium size depending on the size of applied frequency [70]. The bubbles finally collapse after few cycles, and act as local hotspots, with temperature of 5000 K and pressure of 1000 atm. [152]. Such huge amount of mechanical and thermal energy is sufficient for causing exfoliation of nanotubes. Collapsing bubbles produces a shockwave causing “peeling off” which finally, results in separated CNTs. Additionally, surface imperfections on the CNTs acts as a nucleation site for these bubbles [70].

Ultrasonic equipment can be classified into two types: bath sonicators and tip (probe) sonicators. Researchers have frequently used bath sonication for dispersing CNTs in organic solvents such as DMF, NMP and methyl ethyl ketone (MEK) [16], [129], [153], [154] and water [155], [156]. However, it has been reported that bath sonication is not adequate for proper dispersion of nanotubes. It can lead to breakdown of larger bundles but individualize CNTs [134], [157]. Probe sonication, on the other hand, has been consistently mentioned as efficient method to separate CNTs from bundles [112]. However, probe sonicator transfers energy efficiently and this leads to shortening of nanotubes [70]. During initial experiments of this study, it was observed that bath sonication (100 watts) is not adequate for dispersion of pristine CNTs in water. Bath sonication was able to break big agglomerates, but was unable to disperse CNTs finely, indicated by significant settling at bottom (even after 18 hours of sonication). TEM was used to characterize the quality of dispersion. Figure 2.11 presents the TEM images representing the dispersion state of CNTs with both type of sonication equipment. The images confirms that heavy agglomerates are present in samples prepared from bath sonication. On the other hand with probe sonication (power was toned down to 70 watts to facilitate temperature control and reduce noise), 50 minutes of sonication was sufficient to completely exfoliate CNTs as confirmed by Figure 2.11 (B). The CNTs are well separated and no ag-

glomerates are present. The effectiveness of probe sonication was further confirmed by UV visible spectroscopy and visual observation.



(A). 18 hours bath sonication ***(B). 50 minutes probe sonication***

Figure 2.11 TEM images depicting the CNT dispersion state after sonication

2.6.4 Film formation in latexes

Film formation in latexes consists of three stages: drying stage, particle deformation stage and inter diffusion stage. Figure 2.12 makes an attempt to explain the various stages in process of film formation of latexes. In drying stage, water evaporates from the film and particles are restricted to a particular space. During this step the particles start ordering themselves. Vdw forces starts acting as the distance decreases further. It has been calculated that vdw forces are proportional to r^{-6} [158]. At a particular point, the magnitude of force reaches a critical value and particles coalesce and deform to form a irreversible film. This phenomenon is also explained by Figure 2.13. It can be observed that vdw are quite significant at very low intermolecular distance. At particular intermolecular distance, even the highly stable colloidal systems are bound to collapse. This marks the end of particle deformation stage. Finally, interdiffusion stage involves diffusion of polymer chains within the particles to achieve cohesive strength and a clear film is formed [159]. An important aspect of film forming in latexes is minimum film forming temperature (MFFT), which is defined as lowest temperature at which the polymeric dispersions are able to make a homogeneous film. MFFT of polyurethane is reported to be around their Tg (less than 0 ℃) [160].

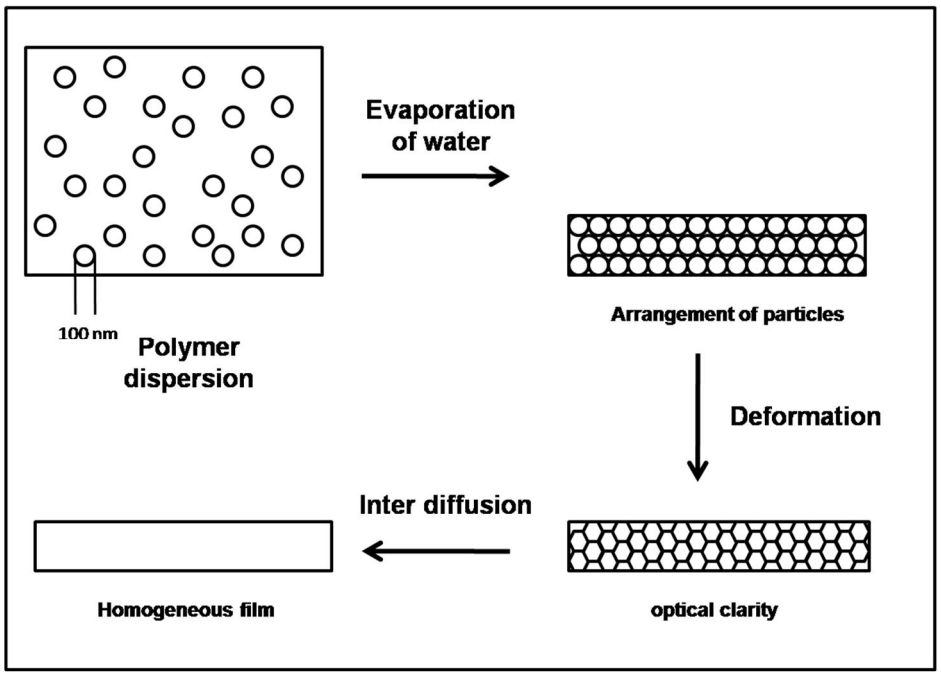


Figure 2.12 Stages involved during film forming in latexes (adapted from [161]***)***

In context to CNT dispersions, it has been reported that adding 0.5 wt% NaCl on solution basis assists creating a well dispersed CNT suspension in latex [162]. However, this method is not used in this study because Cai et al. reported that adding NaCl to latex leads to cracking of matrix, which will be detrimental for mechanical properties of nanocomposites. Moreover, these solid crystals could interfere with the film formation by hindering the diffusion of polymeric chain (stage 3) [160].

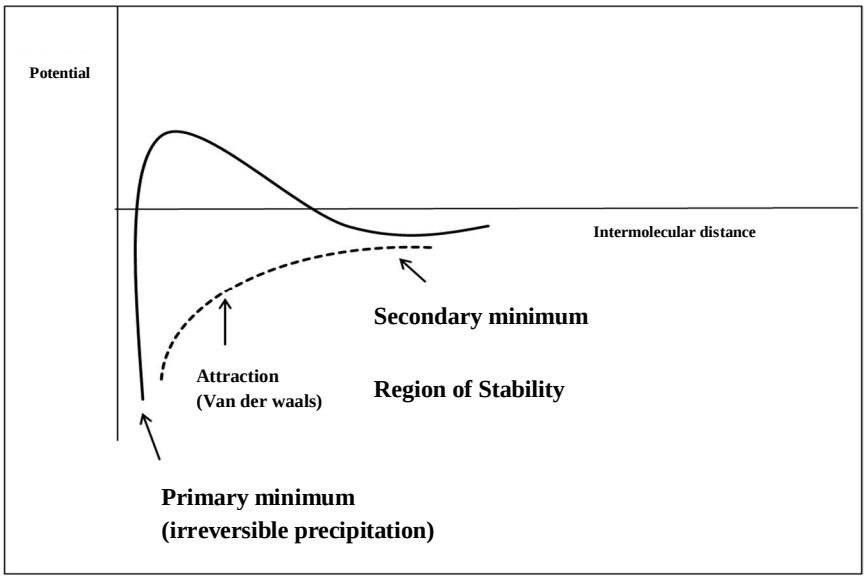


Figure 2.13 Electric potential as the function of distance between molecules in a stable colloidal system (adapted from [163]***)***

Jin et al. has studied the surface morphology of CNTs on the dispersed polymer particles. Figure 2.14 presents image that provides information about arrangement of CNTs on polymer surface in dispersions. It has been hypothesized that the surfactant molecules act as a link between nanotubes and microspheres resulting in hydrophobic interactions which enhances the contact at interface. They also reported that the adhesion of nanotubes is high; even after sonication, the adsorbed nanotubes maintained their adhesion on the surface of PS microspheres. This image can help us understand why latex technology is such an efficient method to process CNT filled nanocomposites. The CNTs (few microns in length) will wrap around the polymer particles as shown in Figure 2.14. During coagulation and deformation stage, the CNTs will trap to between particles and diffusion of polymer chains will take place around them. Therefore, they are likely to form a well dispersed nanocomposite. Figure 2.15 presents the nanocomposite formation from CNT-latex dispersion.

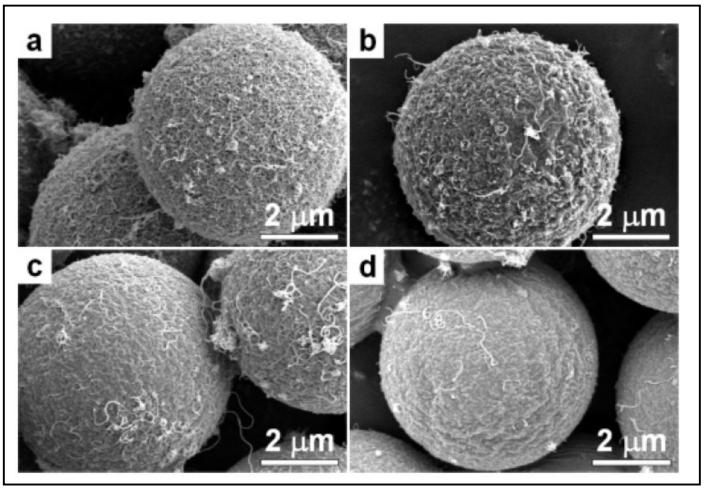


Figure 2.14 FESEM image depicting the arrangement on CNTs on the latex particles; (Copyright [164]***, reprinted with permission from American chemical society)***

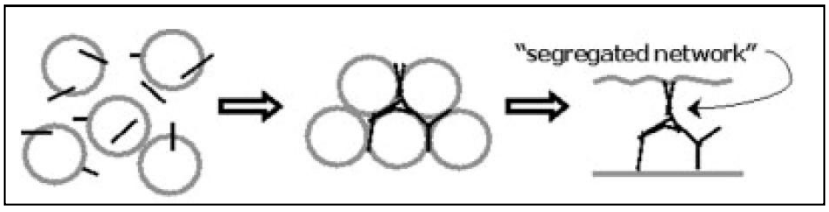


Figure 2.15 Film formation in CNT filled latexes(Copyright [115]***, reprinted with permission from John Wiley and Sons)***

It should be kept in mind that Figure 2.14 depicts polymer particles in microspheres which settle down at the bottom after some time and most commercial latexes are of nanometre range [164]. However, the absorbing mechanism is not likely to change as

adhesion between nanotubes and polymer particles will be increased; the smaller spheres will have more surface area and therefore, will attract more nanotubes.

2.7 Characterization of CNT dispersions and polymeric nanocomposites

This section consists of techniques that are popularly used to characterize CNT dispersions and nanocomposites. The basic idea behind characterization is to probe a material and measure the response of material against it. Such techniques allows to relate material properties with structure, processing parameters and ultimate performance of materials in use [165]. Additionally, they provide vital data needed to replicate the material. Choosing a correct technique to characterize is one of the most critical elements for research and development of advanced materials.

Characterizing a material consists of following aspects:

- Assessing chemical and physical properties [165].
- Determining of structure at atomic and microscopic level [165].
- Analysis of defects and impurities [166].
- Analysis of compositional and chemical homogeneity [166].

For nanocomposites, CNTs are characterized during its entire lifecycle, from powder state in reactors to its final position as nanofillers in matrix [70]. A proper evaluation is essential for reproducible results and standardizing the process. In context to latex technology, stable dispersions are most critical ingredient. Therefore, such dispersions need to be accurately analysed for: optimum amount of surfactant, dispersion state, long term stability, and relative comparison among two dispersions. These characteristics provide relevant data for qualitative and quantitative analysis, which is helpful during research and development. Moreover, such evaluations will prove to be handy, when the process is applied for bulk productions, as it gives a fine insight needed for qualitative comparison of production batch with respect to standard and laboratory batches.

Various techniques are available to characterize CNT dispersions. Optical methods such as such as ultraviolet-visible-near-infrared (UV-vis-NIR) spectroscopy, near-infrared (NIR) fluorescence, and Raman scattering often used for such purposes [137]. During literature review for this research work, it was observed that UV visible spectroscopy has recently emerged as an instrumental tool to characterize CNTs in liquid medium. This method is also most commonly used and is valuable due to its quick applicability, simplicity and wide range of interpretable data [18], [44], [112], [155]. Additionally, microscopic evaluations provide valuable results that assists in confirming data obtained by advanced techniques. Transmission electron microscopy (TEM) [112],

Scanning Electron Microscopy (SEM) [4] are well known among researchers for evaluating CNT dispersions. Other methods that can be used includes particle size analysis[146], long term settling studies [132], [167], centrifuge studies [70], [137], [168], [169] and zeta potential measurements [48], [139], [146].

On the other hand, polymer nanocomposites are usually characterized for: quality of dispersion, effect of filler morphology, mechanical properties and effects of process parameters on end products [170]. In their review on polymeric nanocomposites, Lagashetty and Venktaraman, mentions that X ray diffraction, SEM and infrared spectroscopy are the most important methods for nanocomposites [166]. It is worth mentioning that other techniques are also popular, probably because of relatively simple approach and cost efficiency. Thermal analysis is one of those methods which is extensively used for to characterize nanocomposites [127]. It gives fast access to information that is relevant in determining the performance and molecular arrangements of the materials in different environments. Differential scanning calorimetry (DSC) provides data about crystallization and molecular transitions with change in temperature. Thermal gravimetric analysis (TGA) is commonly used to evaluate the thermal stability [166]. Additionally, dynamic mechanical analysis (DMA) is used for evaluating viscoelastic properties [171]. It also provides deep insights about interfacial adhesion between CNTs and matrix and dispersion state.

Stress-strain analysis of polymeric nanocomposites is also popular as it provides valuable information regarding load transfer and is usually used by researchers. Another methods used for characterizing nanocomposites are Fourier Transform Infrared Spectroscopy (FTIR) [128] and raman spectroscopy [172]. The choice of method generally depends on available resources, time constraints and desired application of product. However, it is recommended to use more than one technique in order to obtain more precise results.

2.8 Recent advances in CNT filled nanocomposites

As mentioned before, researchers have predicted that nanocomposites are probably the first area, where CNT technology is going to make a significant impact. This claim appears to be valid as there are many commercial products available as additives in the markets. One of such product is TUBALL®, launched by OCSiAl. The company itself has recently gone through a merger with ZYVEX technologies and is presently considered as largest nanomaterial company in the world. This product has been marketed as universal nanomodifier of materials. This product is different from other similar products in market as impurities are encapsulated in carbon shells. Moreover, company claims that TUBALL® is 50 times cheaper than similar products available in market. According to the website of company, this product makes nanotubes commercially viable product for the very first time [173], [174].

Another major progress is reported in the field of conductive inks by Linde nanomaterials [175]. They have developed a new technology for dispersion of nanotubes that does not require sonication or functionalization; hence, CNTs are not damaged and the aspect ratio is preserved. This can be a ground-breaking technology as it provides solution to one of the major challenges of CNT filled nanocomposites; avoiding use of sonication, which is one of the most efficient methods reported to disperse nanotubes in polymeric matrix. They have termed it as salt-enhanced electrostatic repulsion (SEER) process. In this process, individual CNTs in dimethyl sulfoxide solution are produced by reducing carbon nanotubide salts. Such inks are already available in market and versatile in terms of application. They can be deposited by any conventional application technique including printing, spin coating and spray coating.

CNTs have indeed advanced to higher stages since we found about their existence. They are presently used in cycles that run in tour de France and protecting spacecrafts via ESD shields [3]. They are slowly and steadily moving towards commercialization, which the studies suggest will surely happen within next decade.

3 Experimental

CNT filled PU nanocomposites were evaluated for electrical and mechanical properties in the current study. Latex technology was used for processing of nanocomposites. CNT dispersions were prepared by sonicating four different kinds of CNTs in aqueous surfactant solution. Power of sonication was kept as low as possible; in order to minimize damage to CNTs. CNT dispersions were characterized by TEM, SEM and UV visible spectroscopy. All the dispersions were mixed with polymeric latexes and casted in glass petri dish to get nanocomposite films of around 800 µm. Nanocomposites were characterized by tensile testing, DMA analysis and electrical testing.

3.1. Materials

3.1.1 Polymers

Anionic aliphatic polyester-polyurethane (PE-PU) dispersion, Bayhydrol UH 240 and Impranil DLN, were used in this work. Both the polymers were kindly supplied by Bayer Materialscience, Finland. Characteristics of polymer dispersion are provided in Table 3.1 (as provided by manufacturer [176], [177]). PU was selected for this study because it is a versatile polymer currently being used in wide range of industrial applications such as adhesives, coatings, elastomers, footwear, foams and automotive finishes. This makes PU one of the most popular polymers in terms of commercial applicability. On the hardness scale, it fills the gap between rubber and plastics. It can be prepared from hardness extending from 20 Shore A to 85 Shore D [178]. Such a range of hardness is main advantage that makes it suitable for numerous applications.

Table 3.1 Characteristics of polymers used in this study

Property	Bayhydrol UH 240	Impranil DLN
Non-Volatile content	40 +/- 1 wt%	40 +/- 1 wt%
pH	7 +/- 1	6.5 +/- 1.5
Flow time at 23°C, 4 mm cup	< 70 sec.	< 70 sec.
Appearance	white dispersion	white dispersion
Density @ 23°C	~ 1.1 g/cm^3	~ 1.1 g/cm^3
Average particle size	210 nm	Not available

3.1.2 Carbon nanotubes

CNTs used in this research were provided by Oxford University, UK under the code name EoDo3 and BNC878BIG. A major characteristic of these nanotubes was their highly aligned extra-long nature (order of mm), which can be easily observed in Figure 3.1. The detailed characteristics of nanotubes are listed in Table 3.2. Two different commercial CNTs were also procured for this study; Nanocyl® NC 7000 (NC 7000) and Baytubes® C 150 P (C150P). The basic idea behind choosing commercial CNTs was to evaluate comparative performance of nanotubes prepared by Oxford University against a standard product and imply the commercial viability, if any. NC 7000 and C150P were selected because they are widely reported MWCNTs in literature [6]. Figure 3.2 provides insights into their structure which will further help in analysing their behaviour in polymeric matrix. The structure of NC 7000 is described as loosely packed "combed yarn" structure, while C150P is referred to as "bird nest" with smaller tightly held agglomerates [6].

NC 7000 was kindly supplied by Belgium nanocyl s.a., which are produced by catalytic carbon vapour deposition (CCVD). The producers recommends that these nanotubes are advantageous for application demanding low percolation threshold such as dissipative plastics and coatings [179]. Manufacturers also claims that they have low defect density and are most conductive nanotubes present in market today [180]. C150P was provided by Bayer materialscience, Germany. They are also prepared by a special high yield CCVD process, which results in high carbon purity [181]. Table 3.2 also enlists the characteristics of NC 7000 and C150P, as provided by manufacturer in the datasheet.

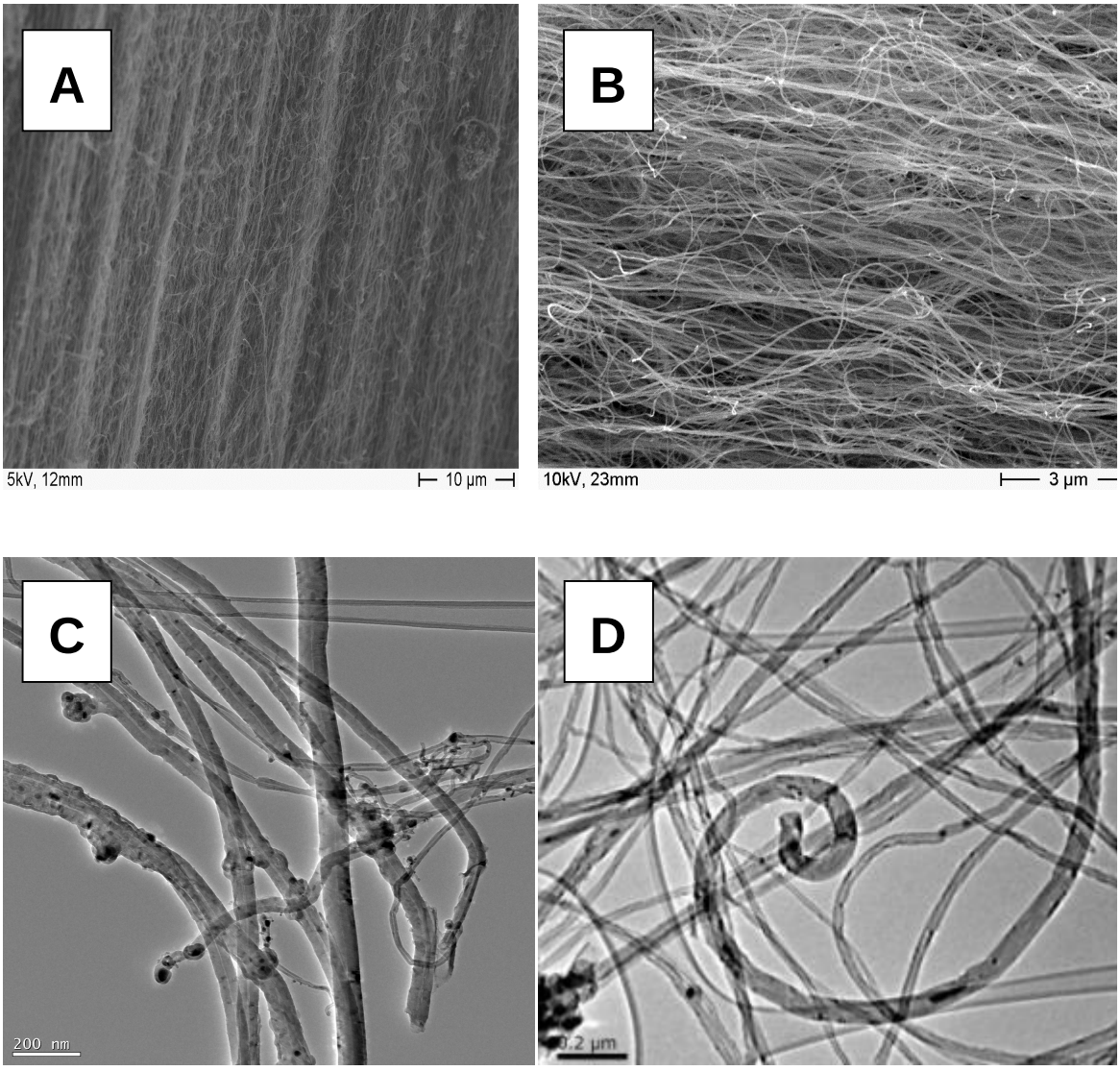


Figure 3.1 Microscopic images of prepared nanotubes: (A) SEM image of EoDo3 (B) SEM image of BNC87BIG (C) TEM image of EoDo3 (D) TEM image of BNC878BIG

Table 3.2 Characteristics of nanotubes used in this study

Property	EoDo3	BNC878BIG	NC 7000	Baytubes C150P
Diameter	40-60 nm	30-50 nm	9.5 nm	~13 nm
Length	500-1000 µm	300-800 µm	1.5 µm	>1 µm
Raman ID/IG	~ 0.4	~ 0.3	not available	not available
Residual Fe:	~ 3 wt%	5-6 wt%	~ 10 wt%	~ 5 wt%
TGA T50%	~ 600 °C	600-620 °C	~ 580 °C [153]	>800 °C

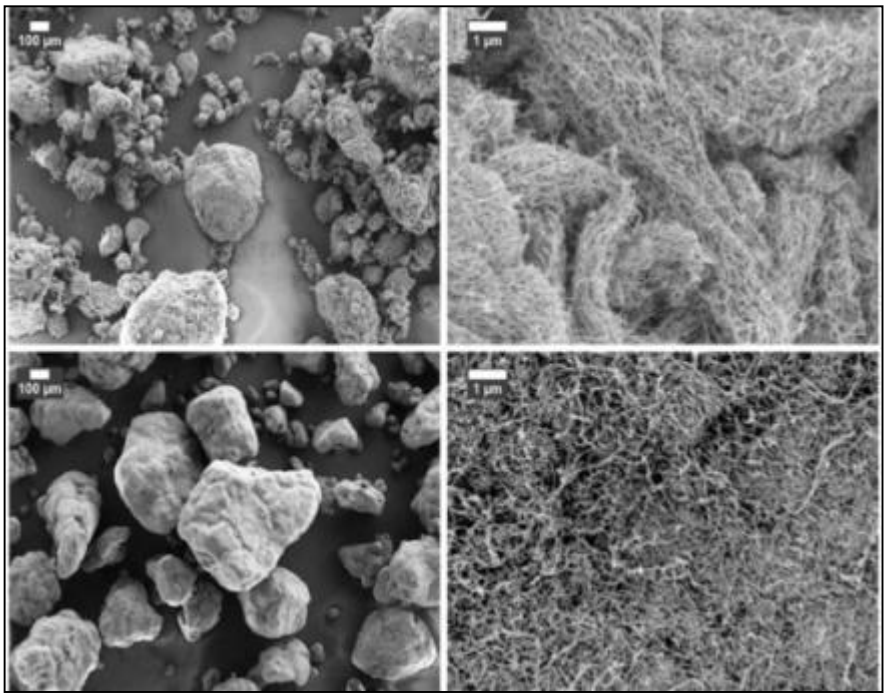
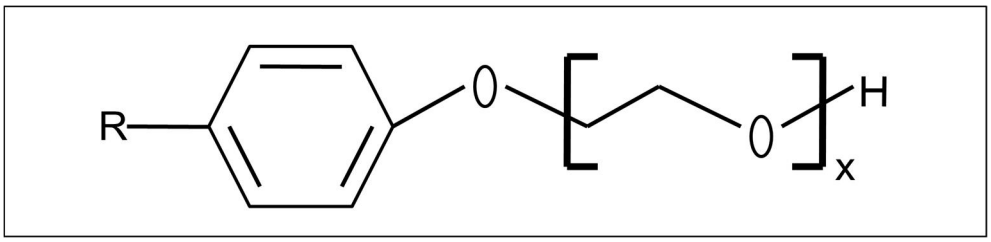


Figure 3.2 Magnified images of nanotubes: Nanocyl NC 7000 (top) and Baytubes C150P (bottom)(copyright [6]***, reprinted with permission from Springer)***

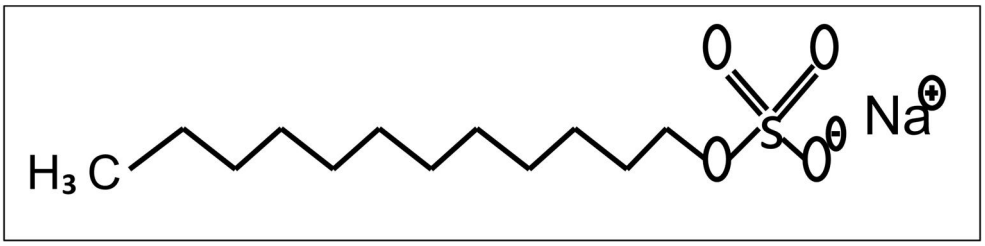
3.1.3 Surfactants

Three surfactants were carefully selected for this thesis work. Triton X 100 (TX100), an non-ionic, octylphenol ethoxylate surfactant, was used for morphology study as it has been reported as most popular and efficient surfactant by researchers [18], [48]. The structure of TX100 is presented in Figure 3.3 (A); the hydrophobic octyl group is adsorbed on the surface of CNTs and hydrophilic segment stabilizes the CNTs in water [167].

In surfactant study, a new eco-friendly surfactant Dabco DC 193 (DC193) was compared with popular commercial surfactants: sodium dodecyl sulphate (SDS) and TX100. SDS is popular anionic surfactant having the structure described in Figure 3.3 (B). On the other hand, DC193 is a silicone based surfactant known for its chemical inertness. SDS (90 wt%) and TX100 were procured from VWR International, Finland; DC193 from Air products, Finland. Table 3.3 presents the composition of DC193 as reported in materials safety data sheet [182].



(A)



(B)

Figure 3.3 Chemical structure of surfactants: (A). TX100 (B). SDS

Table 3.3 Composition of DC193

Component Name	wt%
Dimethyl, methyl(polyethylene oxide) siloxane	70.0 - 90.0
Polyethylene oxide monoallyl ether	10.0 - 30.0
Polyethylene glycol	5.0 - 10.0

3.2 Sample preparation procedures

In order to minimize the errors during reproducibility of results, all the parameters such as glass wares, depth of sonication probe in liquid medium, volume of dispersions and other physical parameters were kept same for a particular study. Nanopure water with resistivity >18 MΩ cm was used for all the experiments.

3.2.1 Purification

CNT usually contains some impurities in the form of metal catalysts which are embedded in them during preparation. These impurities can be as high as 30 wt% for CNTs prepared from arc discharge method [112]. Such impurities can be removed by the methods such as acid oxidation, gas oxidation or filtration [78]. However, most of these methods utilizes treating with oxidative acids which results in damage to CNTs [78]. Furthermore, these techniques are usually expensive and accounts for big capital investment for large scale processing. The CNTs used in this study are of high purity (>90%). Therefore, it was decided that CNTs will be used in pristine form, as the favourable results would be advantageous for commercial applications as it will save capital and time delay in finished products.

3.2.2 Ultrasonication

In the initial experiments, it was found that bath sonication is not sufficient for proper breakdown of the CNT agglomerates. Additionally, the power provided by bath sonicator is difficult to quantify as it is depends on shape, thickness and volume of the vessel. This might lead to complications in reproducing results. Therefore, tip sonicator was selected for preparing nanocomposites. Temperature was controlled by dipping vials in ice water during sonication. Temperature control is necessary because sonication results in overheating of liquid and rapid increase in temperature can cause significant effect on organic molecules of surfactants.

Soniprep 150 plus equipment was used for dispersing CNTs in water. All the samples were sonicated with titanium alloy tip of 9.5 mm diameter. The frequency of the sonicator was fixed at 23 kHz but the power was changed according to requirements. For morphology study, power was kept at 20 watts as it was extremely important to disperse the CNTs with minimum damage. On the other hand, for surfactants study, the power was fixed at 70 watts as it was observed that C150P were taking too much time to disperse at lesser power.

3.2.3 UV visible spectroscopy measurements

UV visible absorbance can provide valuable information needed for qualitative and quantitative analysis of dispersions [70]. It has been reported that all CNTs are active in UV-visible region due to presence of 1D van Hove singularities [183]. CNTs of different diameter and chiral vectors (C_h) produce a finer structure of bands which superimpose to form characteristic spectra. On the other hand, bundled CNTs are negligibly active in this range. The difference in behaviour of bundled and individual CNTs can be used to determine the quantity of individual CNTs in the suspensions [70]. The relation between CNT concentration and the height of absorption spectrum is given by Beer Lambert's law**,** according to it:

$$A = \varepsilon l c \qquad \textit{Equation 3.1}$$

Where, ε is molar absorbtivity of the solution; l is path length; c is concentration. Therefore, absorbance value of dispersion is directly proportional to concentration of CNTs present in it. This relation can be used to evaluate various properties of CNT dispersions. UV visible spectroscopy is emerging as cheap and effective technique to characterize CNT dispersions. It has been successfully employed for following evaluations :

- Optimum sonication time/energy [112].
- Optimum surfactant concentration [18].
- Maximum CNT concentration for stable dispersion [44].
- Long term stability study for CNT dispersions [183].

- Comparison of surfactants efficiency [18].
- Determination of concentration of CNTs in dispersions [18], [155].

In this study, UV-visible spectra were measured with Shimadzu UV-1601 UV-VIS spectrometer. The spectra were recorded after diluting samples, from 250nm to 500 nm with the sampling interval of 0.2 nm. The dispersions were diluted order to reduce the equipment error [112].

3.2.4 Optimum surfactant concentration

The concentration of surfactant is the critical for producing a stable dispersion of CNTs in water; stable dispersions generally mean that CNTs are present in separated state or aggregates of few in medium for a long time. In latex technology, the amount and quality of surfactant determines the degree of dispersion in medium and nanocomposites [44]. In fact, surfactants can be termed as most decisive component for a stable dispersion. If the surfactant is present in less than required concentration (critical or optimum amount), CNTs separated from bundles by sonication will not be covered with enough surfactant molecules; hence, will agglomerate due to influence of van der Waals forces. On the other hand, surfactant presence in excess will leave them unused in the solution. Apart from causing increase in cost of product, they are likely to form micelles. Furthermore, they will act as plasticizer in finished polymer composites and lead to diminished mechanical properties [148]. Therefore, surfactants should be present in optimum amount; no more, no less.

Recently, considerable amount of studies have been published that determines the optimum surfactant concentration for producing a stable dispersion of CNTs in water [18], [39], [70], [184]. The basic concept behind the process is to subsequently increase the surfactant concentration while keeping the CNT concentration constant. All the samples are sonicated for fixed time and UV visible absorbance is determined at particular wavelength. The sample with maximum absorbance will have highest concentration of CNTs and thus will have better stability than others. A bell shape curve is expected, which is shown in Figure 3.4.

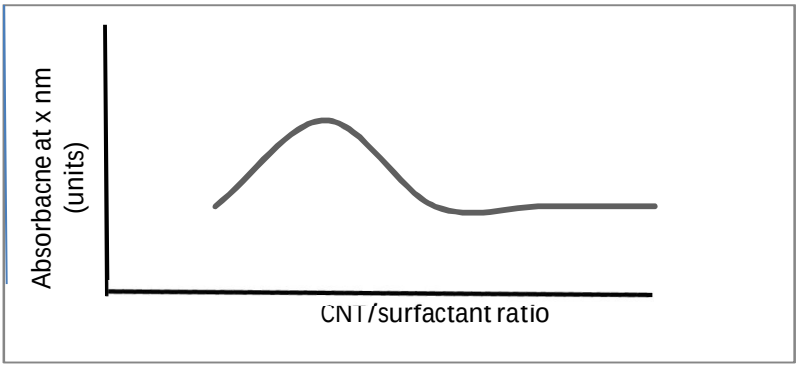


Figure 3.4 Standard graph for determination of optimum surfactant concentration (adapted from* [18]*)

In this study, optimum surfactant concentration was determined only for trials concerned with surfactant study. The same process was followed as mentioned above. Experiments were carried out by varying the surfactant concentration with CNT concentration as constant. CNT concentration was kept at 0.2 wt% and concentration of surfactant was varied from 0.2 wt% to 0.6 wt% with an increase of 0.1 wt% in each trial. An exceptional trial was done in the case of TX100 at 0.15 wt% concentration. UV visible spectra were collected from 500 nm to 250 nm with the scanning speed of 100 nm/min at interval of 0.5 nm.

3.2.5 Optimum sonication energy

During dispersion of CNTs, sonication imparts massive amount of energy to medium. This energy is adequate to create local hot spots with temperature around 5000 ℃ and pressure of 1000 atmospheres [152]. Such conditions are sufficient to cause damage to the CNTs in the form of shortening and local disruptions [37]. On the other hand, if adequate energy is not provided – the CNTs will not be separated from bundles, which will affect performance of nanocomposites. Therefore, it is essential to minimize this damage without compromising with proper dispersion state.

UV visible spectroscopy can be used to determine the optimum energy required for creating a stable dispersion. It allows to monitor the degree of dispersion in real-time and indicate when to stop the sonication. Grossiord et al., in their research, elaborated this versatile and easy method [112]. As described in previous section, in contrast to behaviour of bundled CNTs - individual CNTs shows cumulative activity in UV visible region. This implies that the value of absorbance of CNT dispersion will increase with sonication energy. A standard expected graph is shown in Figure 3.5. The plateau value represents the maximum achievable exfoliation.

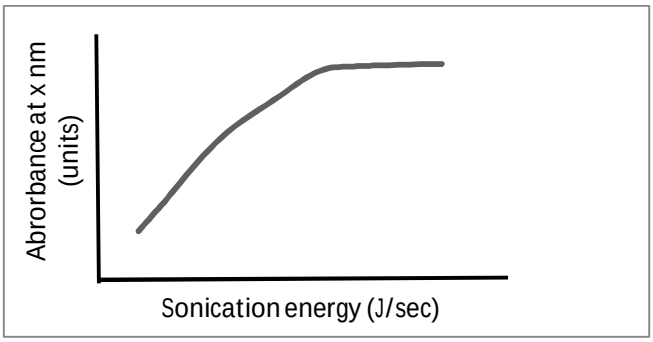


Figure 3.5 Standard graph for determining optimum sonication time (adapted from* [112]*)

For morphology study, 0.6 wt% CNT was dispersed in 1.2 wt% solution of TX100 in water. The power of sonication was kept constant at approximately 20 Watts, to minimize the damage to nanotubes. On the other hand, for surfactant study- 0.4 wt% of CNTs was added to 15ml of aqueous solution containing 0.8% DC193 surfactant and sonicated at power of approximately 70 Watts. Samples were taken regularly during the sonication. UV spectra were recorded after diluting samples by a factor of 650, from 250nm to 500 nm with the sampling interval of 0.2 nm. The dispersion was diluted to achieve absorbance less than one unit, in order to reduce the error caused by spectroscopic measurements.

3.2.6 Optimum CNT concentration

It has been reported that for a particular surfactant-CNT couple, there is a maximum CNT concentration that can be held by dispersion [70]. Excess amount of CNTs in solution leads to agglomeration and poor state of dispersion. Therefore, the CNT concentration should be carefully selected. For this work, the value of maximum concentration was selected according to data available in literature. It has been reported that maximum CNT concentration that can be hold by water is 1.4 wt% [111]. In this study, the CNT concentration in dispersions is kept well below this value (less than 1 wt%).

3.2.7 Preparation of aqueous CNT dispersions

Figure 3.6 presents the process flow used for preparing CNT dispersions. It is worth mentioning that for morphology study, concentration of surfactant (TX100) was kept constant at 2:1 in all the trials as focus was on properties of CNTs. This was done in order to eliminate the effect of surfactant on properties of nanocomposites. Samples were prepared by sonication until the maximum exfoliation of CNTs was achieved. The method is based on research work of Grossiord et al. [112] and reported in section 3.2.2.

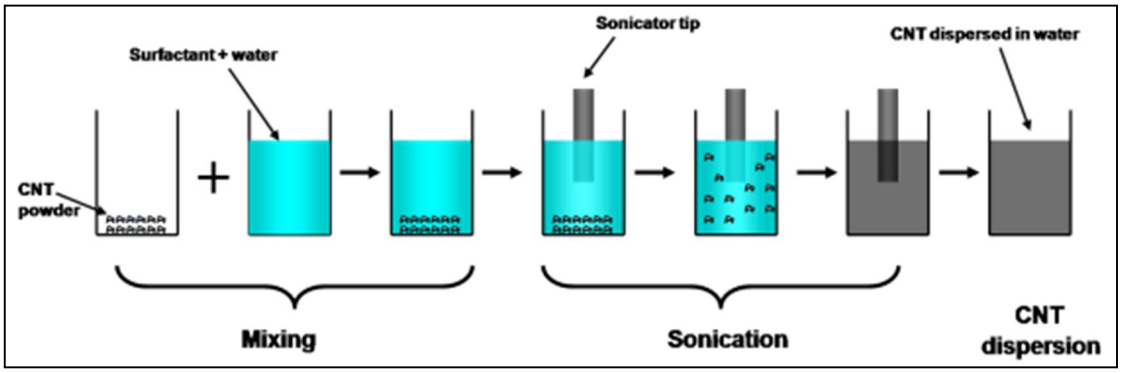


Figure 3.6 Process chart depicting the preparation of CNT dispersions

3.2.8 Long term stability study

Long term stability is an excellent approach to determine and compare the effectiveness of surfactants. This method is of high commercial interest and already been in use for products such as paints, adhesives, latexes and other finished products. The data obtained from this method can be used to determine the shelf life and predict the behaviour of product during transportation. Traditionally, visual inspection was frequently used to characterize products. Even now, micro dispersions are evaluated on the basis of settling at the bottom of container. Heavy settling in short period of time indicates that fillers agglomerated indicating the lack of stability in dispersions. Visual inspection can be used for nano dispersions as it can reveal the important details about macroscopic agglomeration [132]. However, visual inspection does not provide quantitative information on agglomeration at nanoscale. Therefore, advanced techniques are required for lucid understanding of nanoscopic agglomerates. Once again, UV visible spectroscopy is an instrumental tool in determining long term stability [183]. As mentioned in section 3.2.3, UV-visible absorbance is a precise technique to determine the concentration of CNTs in the suspensions. A constant value of absorbance over a long period of time (weeks or months) would mean that concentration of CNTs is constant, which further imply that CNTs have not re-agglomerated. Figure 3.7 presents the expected graph of absorbance values over long period of time for stable CNT dispersions. This method is successfully employed by many researchers for studying the long term behaviour [111], [139], [185].

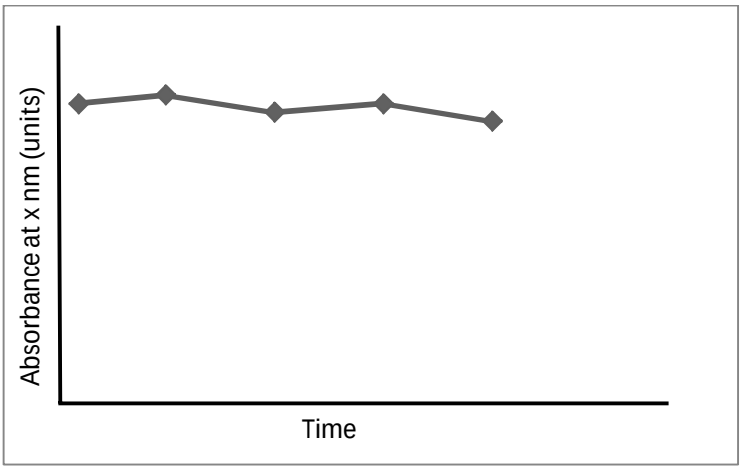


Figure 3.7 Standard graph for long term stability study for stable CNT dispersions (adapted from [185]***)***

In order to prepare samples for long term stability, CNT dispersions were centrifuged at 3000 rpm for 30 minutes to remove impurities such as metal catalysts, which were embedded in CNT powder during production. 80 percent supernatant was carefully collected from the top and stored in separate vial. Samples kept undisturbed at room

temperature for long time (few weeks to months). Apart from visual observations, UV visible absorbance values were collected over regular time intervals. For UV visible spectroscopy, samples were prepared by collecting a 200 µml droplet and diluting it to the factor of 90 before recording a UV visible spectrum between the wavelengths of 500 nm to 250 nm at the scanning speed of 100nm/min. A constant value of absorbance was expected, which implies that CNTs are still in dispersed state.

3.2.9 Microscopic evaluations

It has been demonstrated that microscopic techniques are helpful in controlling and monitoring the status of CNTs at all stages of preparing nanocomposites. Moreover, such techniques are known to provide thorough insights into parameter control, which is required to optimize the performance of nanocomposites [186]. Additionally, microscopic images confirm the data provided by other techniques. For example, the maximum exfoliation time obtained by UV visible spectroscopy can be confirmed by microscopic images that CNTs are indeed separated at molecular level in the given time [112]. Numerous studies are available that have benefited from microscopic techniques such as scanning electron microscopy (SEM) [4], [45], [91], transmission electron microscopy (TEM) [8], [18], [112] and atomic force microscopy (AFM) [9], [38], [39], [91] to evaluate and characterize CNTs and CNT derived materials.

In this study, SEM and TEM were used for imaging of dispersed CNTs. TEM was an instrumental tool in confirming that CNTs are separated in dispersions. SEM, on the other hand, was used to calculate the aspect ratio of dispersed CNTs. Samples were prepared by dropping a droplet of CNT dispersion on a copper grid (300 mesh) with a holey carbon film and air dried for 24 hours. Jeol JEM 2010 Transmission electron microscope (TEM) equipment was operated at 200 kV for imaging of samples. For SEM**,** Field Emission Gun (FEG) Scanning Electron Microscope (SEM) procured from Zeiss ULTRAplus (Germany) was operated at 3.00 kV, with an InLens secondary electron detector. Length of CNTs after dispersion was determined by measuring length of 50 CNTs by using imageJ image analysis software and taking as average. It was assumed that diameter of CNTs was not affected by sonication as it would mean that an entire layer was removed.

3.2.10 Preparation of composite films

CNT filled PU nanocomposites were produced by the method of dispersion casting in the both part of this study. The method was carefully selected due to its simplicity and compatibility with latex technology. Another advantage of this method is that nanocomposites can be processed at room temperature, which is not possible in other methods such as extrusion and hot pressing. Processing nanocomposites at room temperature

avoids unnecessary chain shortening and polymer damage due to degradation at high temperature. Furthermore, it is an energy efficient technique.

For aspect ratio study, composite films of thickness approximately 800 µm were prepared by solution casting on glass petri dish. The concentration of nanotubes was kept between 0-2 wt%. CNT dispersion was mixed with fixed amount of polymer latex and sonicated with tip sonicator for 15 minutes before casting. After casting, the solution was kept overnight and films were annealed at 110 °C until the weight becomes constant which took 6 hours. This step was necessary to ensure complete removal of water. TGA was used to confirm that water content is approximately 0.24 wt% (Appendix 1). For surfactant study, the films were casted by the similar method as described above. The concentration of nanotubes was kept between 0-0.7 wt%. However, the films were annealed at 125 °C for 3 hours after being kept overnight to ensure complete removal of water. Figure 3.8 shows the steps involved in preparation of nanocomposites.

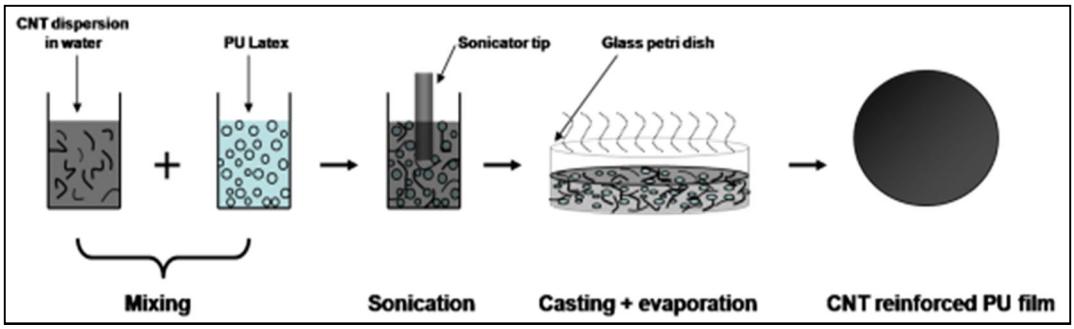
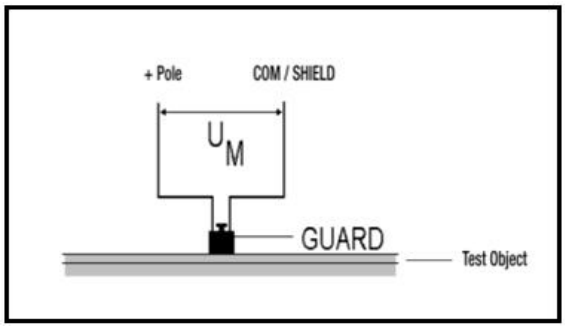


Figure 3.8 Process chart depicting the preparation of nanocomposites

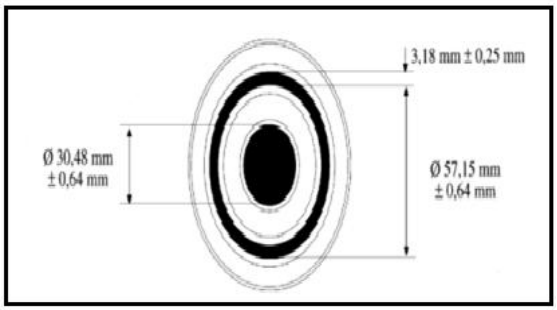
3.3 Evaluation and characterization of nanocomposites

3.3.1 Electrical properties

For polymeric samples, the resistance (or conductance) is determined by measurement of electric current or voltage drop across the sample [187]. In this study, Metriso 2000 was used to measure the surface resistivity; 100 volts was applied through a ring type surface resistance probe electrode (Figure 3.9) on a circular sample of diameter of approximately 10 cm. Volume resistivity was measured for surfactant study, in order to determine the accurate effect of surfactant on electrical properties of bulk nanocomposites. Volume resistance probe was used in a similar way as mentioned above. All measurements were performed at room temperature. For each sample, consecutive data was collected for 5 times and reported as average. Electrical properties are highly dependent on moisture and humidity; therefore, all samples were stored in controlled atmosphere (50% relative humidity and 20 °C temperature) for at least 96 hours before performing measurements.



(A). Voltage application



(B). Top down view of Metriso 2000 surface resistance probe (black region represents electrodes)

Figure 3.9 Surface resistance measurements by Metriso surface resistance probe [188]

3.3.2 Tensile testing

Tensile tests are the most basic type of test performed on materials to evaluate the mechanical properties. It is uncomplicated, fully standardized and relatively economical procedure that provides immediate access to widely recognized property: strength of material [189]. Moreover, this test is valuable quality control tool for testing batch consistency to standard [190]. Tensile testing provide detailed information about mechanical characteristics of material including modulus of elasticity, yield strength, strain behaviour and ultimate tensile strength. However, for highly elastomeric rubbers and polymers (as used in this research), this test is bit different. For example, modulus of a material is reported as stress at a particular strain. However, in rigid materials – modulus is the ratio of stress to strain. Some researchers have used slope of stress strain curve at low strain (less than 5%) as modulus of elastomeric materials [191], [192]. In this study, elastic modulus is also determined in similar way.

It is worth mentioning that polymer used for experimental work of this thesis had high elongation to break; hence, slipping of grips was observed in samples prepared for testing. Furthermore, it was observed that ultimate tensile strength and elongation to

break was difficult to obtain as sample often snapped from the grips before breaking. Tensile tests were carried out using Messphysik midi 10-20/4×11 instrument at room temperature (23 ℃). Crosshead speed was kept at 100 mm per minute. Dogbone (type IV) specimens were made according to ISO 37:2005. Prior to testing, all the samples were kept in controlled humidity of 50% and a temperature of 20° C for at least 96 hours. The Young's modulus was measured in the linear region between 2% and 5% strain.

3.3.3 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is a versatile technique used to characterize materials as function of various parameters such as temperature, time, frequency and atmosphere. In this technique, sample of known geometry is subjected to small deformation (controlled stress or strain) in cyclic manner. For a known stress, sample deforms in a certain amount which depends on its stiffness. DMA measures this stiffness or damping and reports it as modulus or tan delta [193]. It can be used to characterize both thermal and rheological properties simultaneously.

In this study, PerkinElmer PYRIS Diamond DMA equipment was used for dynamic mechanical analysis of the samples. The operational mode was sinusoidal tension/compression with the amplitude of 40 µm and frequency of 1 Hz. The heating rate was kept constant at 3℃/min.

4 Results and Discussions

This section consists of experimental results and relevant discussions derived from the results. This chapter is categorized into two primary subchapters: Morphology and Surfactant study, which are followed by possible sources of errors and general conclusion and future work recommendations.

4.1 Nanofiller morphology study

4.1.1 Effect of sonication

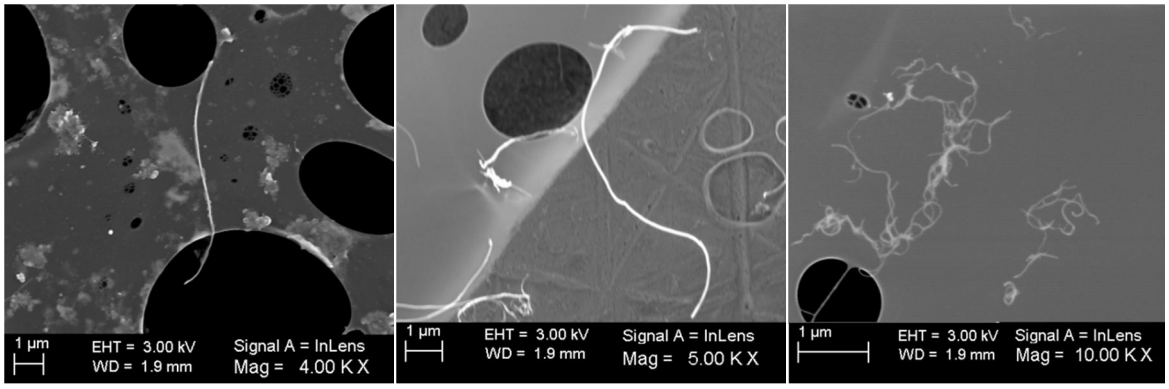
It is well known fact that sonication leads to considerable damage to nanotubes. This study investigated the effect of mild sonication on CNTs by comparing average length of CNTs, before and after sonication. Table 4.1 presents the data indicating the effect of sonication and aspect ratio measurements after sonication treatment. In the future texts, Oxford 1 nanotubes are referred to as AR 110, Oxford 2 as AR 225 and Nanocyl NC 7000 as AR 210 (classified on the basis of final aspect ratio after sonication treatment), for the purpose of brevity. It can be observed that sonication; even at low power, resulted in extreme damage to CNTs. AR 110 got shortened to 5.42 microns from 750 microns of average length. On the other hand, average length of AR 225 CNTs was 8.04 microns from pre-sonication average length 550 microns. However, AR 210 suffered no loss in length (as compared to data provided by manufacturer). One of the possible reasons for that might be lower sonication time (energy) required for dispersion of AR 210. AR 225 and AR 110 took more time (energy) for dispersion because of extra-long and highly aligned nature, which can be clearly observed in Figure 3.1. Additionally, it is apparent that CNTs with large diameters are broken easily. AR 110, with the diameter of 50 nm, shortened by a factor of 140 (approximately). On the other hand, AR 225 which has diameter of 40 nm, got shorten by the factor of 70 (approximately). Our results are in agreement with Heller et al.; who have reported that scission of CNTs, as a result of sonication, is diameter selective. It means that CNTs with thickest diameter are most affected [194]. A possible reason for this behaviour might be increase in stiffness of CNTs due to increase in number of sidewalls.

Table 4.1 Effect of sonication and aspect ratio measurements

Nanotubes	Average length (before soni-cation)	Average length (after soni-cation)	Aspect ratio	Sonication energy imparted
AR 225	300-800 µm	8.04 µm	225	3900 J/ml
AR 110	500-1000 µm	5.42 µm	110	2700 J/ml
AR 210	~ 1.5 µm *	2 µm	210	1500 J/ml

*** provided by manufacturer**

The difference in aspect ratio can be easily visualized in Figure 4.1; AR 225 and AR 110 are more clearly visible with thick thread like appearance; on the other hand, AR 210 appears to be in form of fine filaments having dendritic appearance. Furthermore, it is worth mentioning that all the dispersions prepared for this study were stable for weeks without any sedimentation indicating that CNTs were finely dispersed in water.



(i) AR 225 (ii) AR 110 (iii) AR 210

Figure 4.1 SEM images after sonication treatment depicting the difference in morphology; an interesting observation is significantly visible difference between AR 210 and AR 110, implying the uncertain nature of aspect ratio. AR 210 are short, thin and twisted; AR 110 are thick and straight.

4.1.2 Electrical properties

The electrical resistivity of nanocomposites at different CNT concentration is shown in Figure 4.2. The results clearly indicate that an interconnected conductive network is formed with all three kinds of CNTs as a steep decrease in resistivity values can be observed. The analysis of results strongly indicates that percolation threshold is affected by length of nanotubes. The longer nanotubes (AR 225 and AR 110) have percolation threshold of 0.2 wt%; on the other hand, AR 210 with considerably shorter length has percolation threshold at 0.5 wt%. Furthermore, it is apparent that aspect ratio has no orderly effect on percolation threshold. The correlational analysis of performance (electrical and mechanical) against length and aspect ratio is presented in Figure 4.6 and Figure 4.7. It can be clearly observed that length, not aspect ratio is more accurate in determining the electrical properties. It is worth mentioning that since the CNTs employed in this study are of pristine (untreated) nature, therefore it is expected that electrical properties will further increase when treated and purified to remove impurities [195].

The percolation threshold of non-spherical fillers in matrix is theoretically estimated by concept of excluded volume. According to popular theory, percolation threshold is related to aspect ratio in following way [21]:

$$\varphi_p = \frac{1}{2\,AR} \qquad \textit{Equation 4.1}$$

Where φ_p is percolation threshold and AR is aspect ratio. It has been reported that a good agreement between experimental and theoretical values is observed [38][21]. However, our results contradicts of this theory as they strongly suggest that aspect ratio is not inversely proportional to percolation threshold, rather length of CNTs better fits the pattern. Our results are in agreement with Bai et al., who reported that longer nanotubes results in superior electrical properties in polymeric nanocomposites [196]. The superior dependency of electrical properties on length of CNTs observed in this study can be explained by several premises. First and foremost, smaller nanotubes are likely to have more number of contacts thus resulting in significant increase in cumulative contact resistance. Figure 4.3 attempts to explain why interpreting percolation threshold on the basis of aspect ratio can be misleading. Figure 4.3 is drafted in context to the results obtained with electrical conductivity analysis displayed in Table 4.2. CNTs are drawn to relative scale which is proportional to original scale (mentioned in Figure 4.3). The aspect ratio of CNTs was kept intact while drawing. It can be easily visualized that AR 225, which is the longest are able create an interconnected network with far less

number of nanotubes required. Therefore, resistance in flow of electrons caused by number of junctions will be significantly less in longer nanotubes. It has also been mentioned that longer nanotubes acts as bridges among the small agglomerates thus improving the percolation behaviour [196]. Additionally, diameter also plays a significant role in orientation of nanotubes in polymer matrix. For a given amount of CNT volume, thinner nanotubes will have significantly large amount of nanotubes causing a rise in van der Waals forces due to increased surface area, which can enhance the probability of agglomeration. This agglomeration is likely to result in diminished electrical properties. This tendency of thinner nanotubes to aggregate can be observed in Figure 4.1, where AR 210 are present in entangled state, on the other hand, AR 110 and AR 225 does not exhibit any such tendency. Aggregation tendency of thinner nanotubes with respect to thicker ones has also been confirmed by Dubnikova et al. [197]. Furthermore, it has been mentioned that thinner nanotubes gets twisted during processing which leads to reduction in effective aspect ratio [197] [198]. Finally, aspect ratio is relative quantity and therefore not completely trustworthy. It is very likely that two nanotubes have similar aspect ratio and big proportional difference in length and diameter. Such significant difference in the morphology can lead to conflicting result in polymeric matrix. Therefore, all the above mentioned factors need to considered separately when estimating percolation threshold on the basis of CNT morphology.

Table 4.2 Electrical percolation data of MWCNT-filled nanocomposites

CNT type	Average aspect ratio in matrix	Average length in matrix	Percolation Threshold	Minimum Resistivity (Ω)
AR 225	225	8.04 µm	0.2 wt%	7840
AR 210	210	2 µm	0.5 wt%	78200
AR 110	110	5.42 µm	0.2 wt%	26200

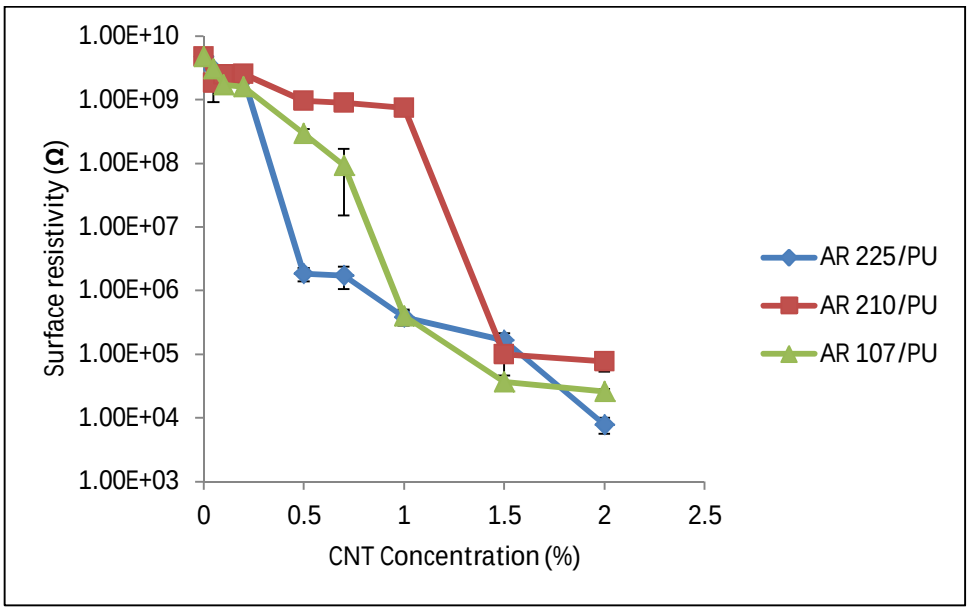


Figure 4.2 Surface resistivity as the function of CNT concentration

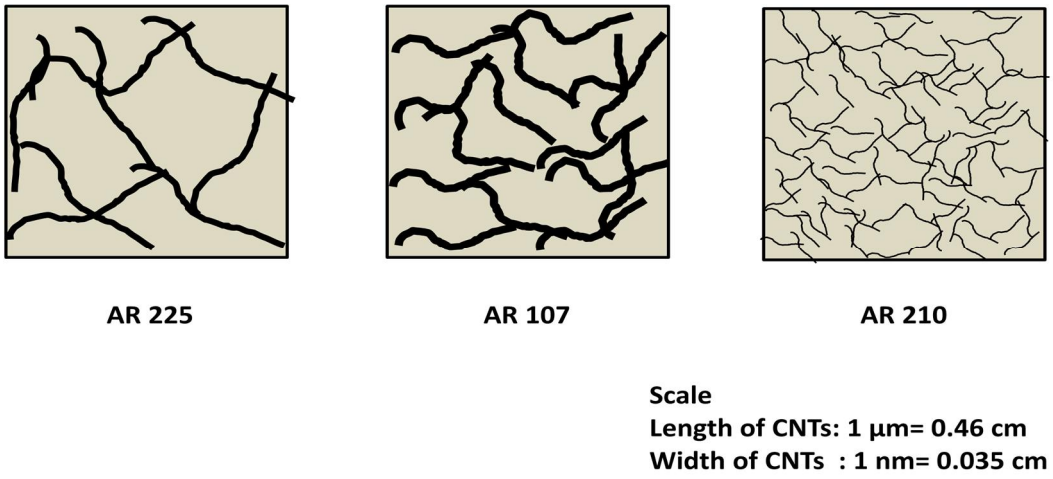


Figure 4.3 Drawn to scale image depicting the formation of interconnected network in polymeric matrix

The conductivity of CNT-filled polymers increased by 5-6 orders in magnitude at 2 wt% concentration of CNTs. The maximum conductivity of all the polymers were in electrostatic conductive range. Our results indicate that latex technology is an excellent method to prepare highly conductive nanocomposites. The percolation threshold achieved in this study is better than significant number of studies reported by other researchers (based on review by Bauhofer and Kovacs) [21]). A possible reason for low percolation behaviour can be the advantage provided by latex technology. Grunlan et al. predicted that during drying of film, CNTs are pushed into the interstitial spaces, which

are generated due to spherical nature of latexes. This leads to decrease in percolation threshold [115].

There are few studies available which have evaluated the performance of CNTs in water based PU latexes. Cai and Song have also evaluated the percolation behaviour of thin diameter nanotubes (8-15 nm) in water based PU latexes. They achieved the percolation threshold of 0.5 wt%. However, They were able to improve conductivity by 4 orders at samples above 1 wt% CNT concentration. On the other hand, our 2 wt% samples were able to display improved conductivity by more than 6 orders [160]. Additionally, they have not mentioned the average length of CNTs, which makes it difficult to compare the results with our findings. A reason for difference in maximum conductivity can be explained by use of different surfactants and possibly different morphology of nanotubes. Tinthoff et al. studied the behaviour of MWCNTs in two component water based PU coatings. Surprisingly, they were not able to achieve good electrical properties, even at 8 wt% of nanotubes concentration. The conductivity of their samples improved by just around 1 order. According to them, a possible reason for this behaviour is extremely fine dispersion state of CNTs in matrix, which results in inability to form a interconnected network. However, no evidence to support this theory was provided [199].

4.1.3 Tensile properties

Results obtained from stress-strain measurements are presented in Figure 4.4. It presents the elastic modulus variation with respect to concentration of CNTs. It can be observed that elastic modulus of nanocomposites is increased with the amount of CNTs. At 2 wt% CNT content, elastic modulus increased by 100% for AR 225/PU, 91% for AR 210/PU and 46.4% for AR 110. The results suggest that higher aspect ratio results in improved elastic modulus. Length appears to have no determining role in this case. The results of correlational analysis of elastic modulus of 2 wt % CNT samples with respect to aspect ratio and length is provided in Figure 4.6 and Figure 4.7. It is clearly indicated that elastic modulus in directly proportional to aspect ratio. AR 225/PU, which has highest aspect ratio also have highest elastic modulus, followed by AR 210/PU and AR 110/PU respectively. Additionally, the elastic modulus appears to be linearly dependent on aspect ratio.

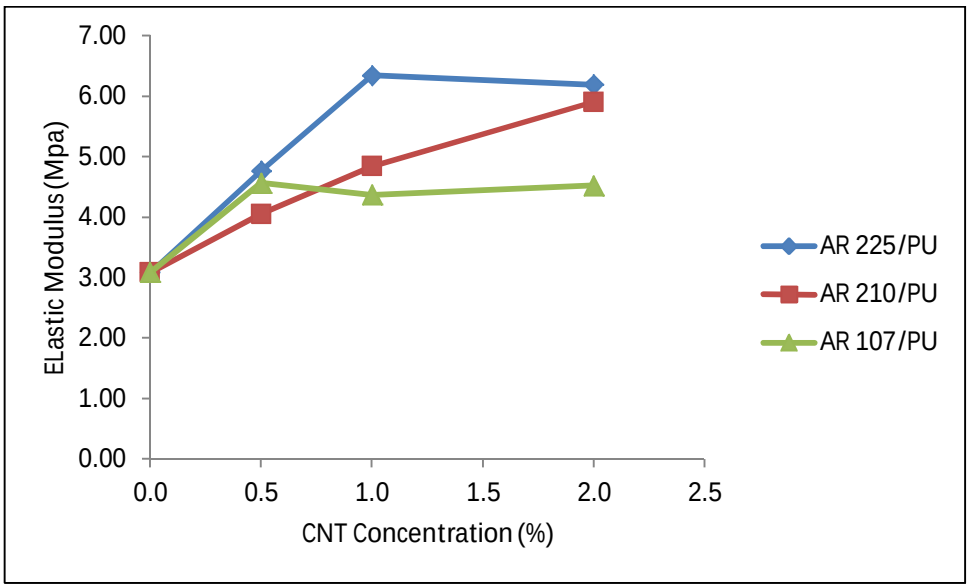


Figure 4.4 Elastic modulus variation with CNT concentration in PU nanocomposites

Tsai-Halpin model was used in order to evaluate the difference in experimental results and theoretical predictions. According to theory, the maximum elastic modulus (assuming uniform distribution and strong interface) can be given by

$$E_c = \left(\frac{3}{8}\frac{1 + 2\,AR\,\eta_l V_f}{1 - \eta_l V_f} + \frac{5}{8}\frac{1 + 2\,\eta_T V_f}{1 - \eta_T V_f}\right) E_m \qquad \textbf{Equation 4.2}$$

in which

$$\eta_l = \frac{E_f/E_m - 1}{E_f/E_m + 2\,AR} \qquad \textbf{Equation 4.3}$$

and

$$\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2} \qquad \textbf{Equation 4.4}$$

Where E_c, E_m and E_f are the elastic modulus of composite, matrix and fibre respectively. AR is aspect ratio and V_f is fiber volume fraction. The elastic modulus of nanotubes was assumed to be 1 TPa. The comparison of theoretical and practical results is presented in Figure 4.5. The results clearly indicate that the theoretical values are considerably

higher than experimental results. This difference can be explained by inability of processing method to achieve CNT dispersion at an individual level. The results also indicate that the difference between theoretical and practical value increases with the aspect ratio. A possible explanation for this behaviour can be the decrease in interfacial strength in high aspect ratio CNTs. However, it is worth mentioning that our results are in disagreement with Ayatollahi et. al, who reported that with higher aspect ratio the difference between theoretical and practical values decreases [28].

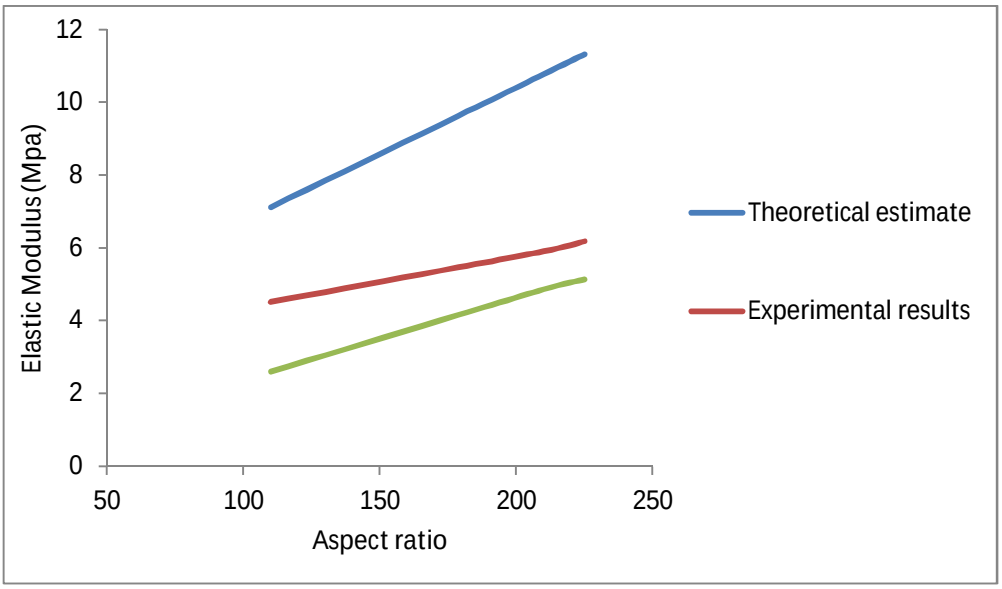


Figure 4.5 Graph depicting theoretical estimate and experimental results for elastic modulus with respect to various aspect ratio

In order to clearly portray the effect of morphology on mechanical and electric properties; both were sketched in the same graph simultaneously with respect to length and aspect ratio. Figure 4.6 presents the variation in tensile properties and electric properties with respect to aspect ratio. Figure 4.7, on the other hand, presents the variation in tensile properties and electric properties with respect to length. A straight line in Figure 4.6 represents the linear variation of tensile modulus with respect to aspect ratio; and the zigzag one belongs to electric properties. Opposite behaviour can be observed in Figure 4.7, where electric properties are proportional to length and tensile modulus follows zigzag pattern.

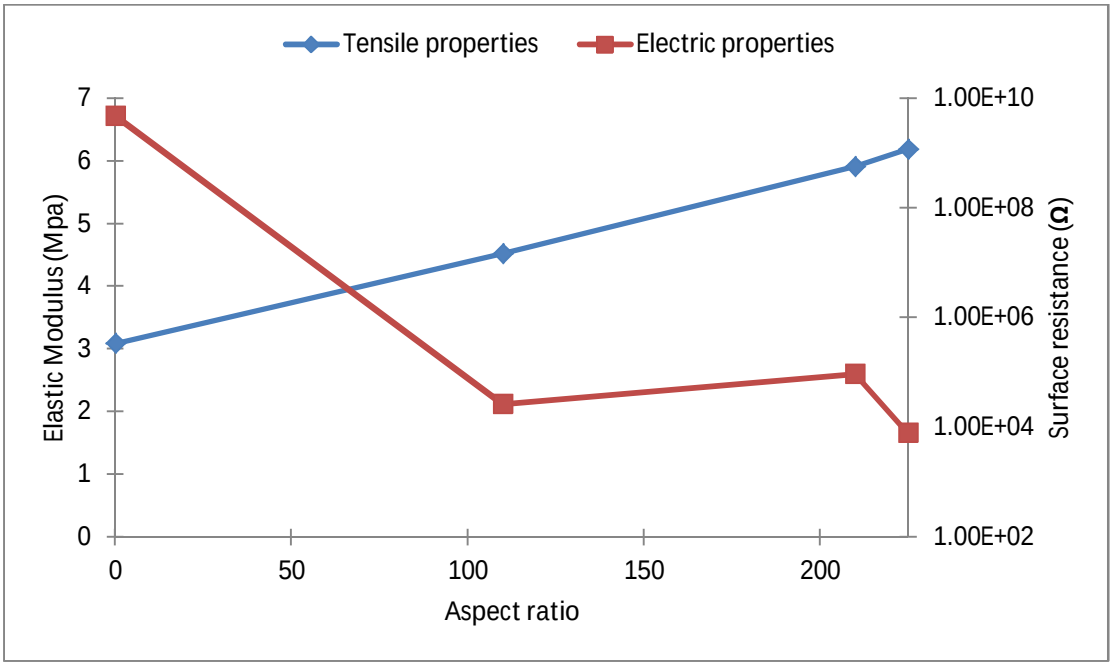


Figure 4.6 Co-relational analysis of tensile properties and electric properties with variation of aspect ratio 2 wt% MWCNT/PU nanocomposites

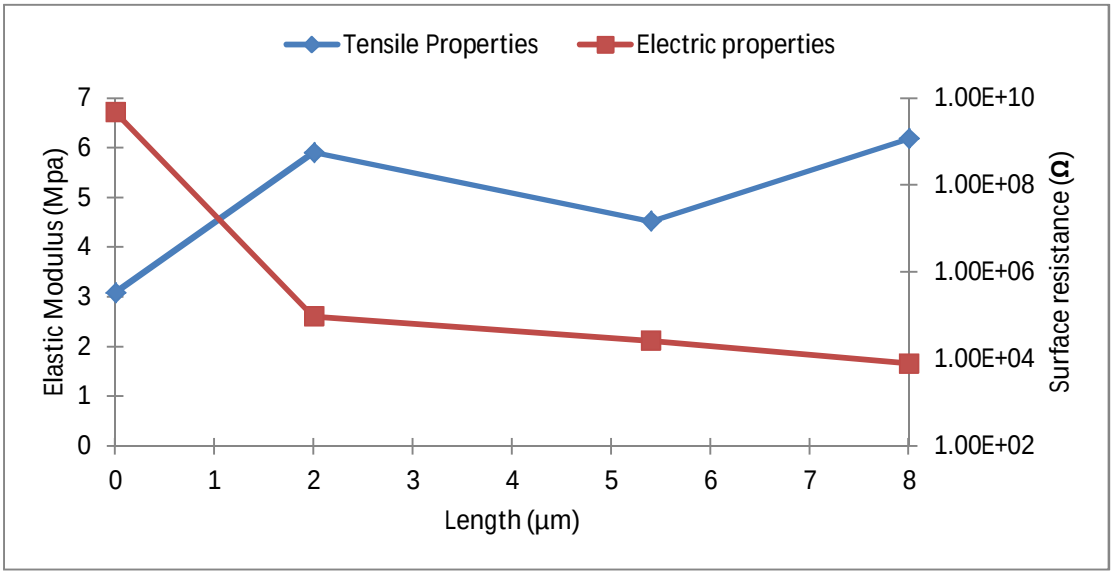


Figure 4.7 Co-relational analysis of tensile properties and electric properties with variation of length for 2 wt% MWCNT/PU nanocomposites

If compared to other studies based on different polymers and processing methods (as reviewed by Spitalsky et al.) the increase in young's modulus of polymer is quite promising [124].

4.1.4 Dynamic mechanical analysis

DMA was conducted in order to confirm the results from tensile testing and to evaluate the quality of interfacial bonding. Furthermore, DMA provides valuable information about mechanical damping ability and thermal footprints in the sample. Dynamic mechanical evaluations of samples with 2 wt% MWCNT content in terms of storage modulus are reported in Figure 4.8. All the samples with CNTs displayed a strengthening effect on PU. This increase in storage modulus is the result of stiffening effect of CNTs and interfacial interactions between CNTs and matrix [200].

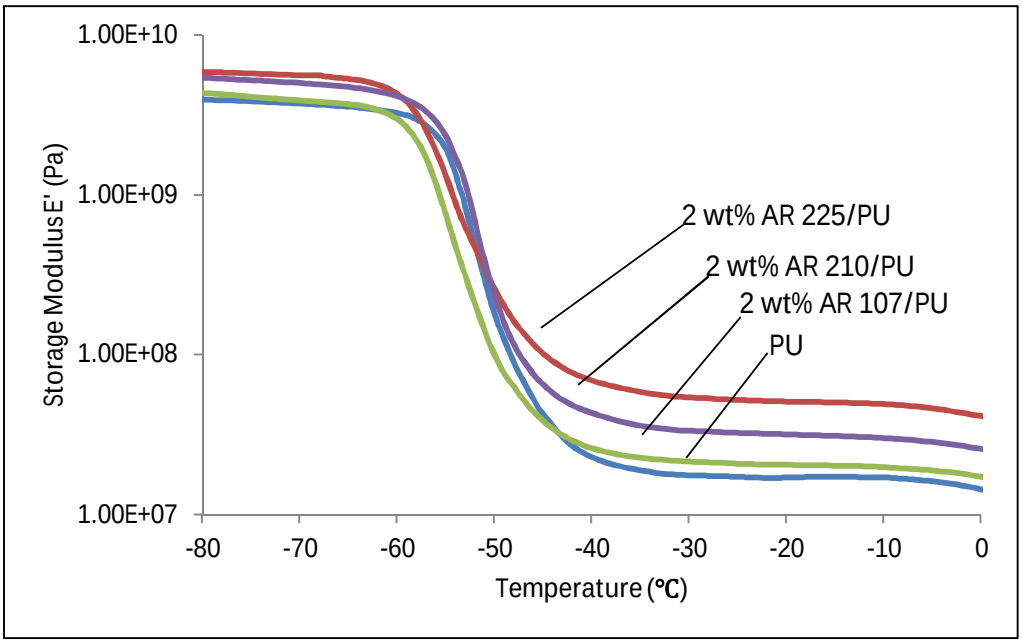
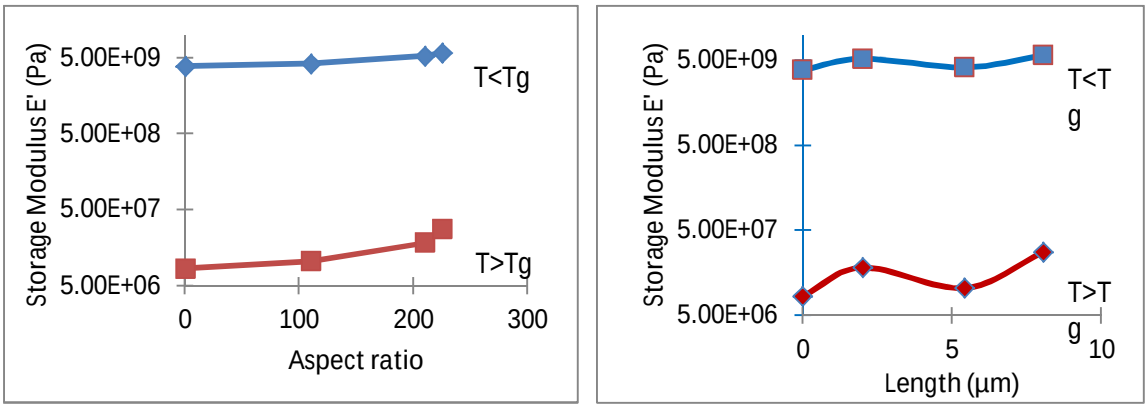


Figure 4.8 Storage modulus as a function of temperature for 2 wt% CNT samples



(i) aspect ratio (ii) length

Figure 4.9 Variation of storage modulus at 20 ℃ (above Tg) and -75 ℃ (below Tg) for 2 wt% MWCNT/ PU nanocomposites

The analysis of results from DMA corroborates the findings of tensile testing. Figure 4.9 presents the images depicting the variation of storage modulus with aspect ratio and length respectively. The pattern in figure strongly indicates that the storage modulus is dependent on aspect ratio and length has no orderly effect on the storage modulus. Additionally, it can be observed from that the storage modulus is not much affected in glassy state as in rubbery region. A possible explanation of this behaviour might be alignment of CNTs under external load. It is well known fact that aligned CNTs have provides better reinforcing properties. In glassy state, material is rigid and CNTs are stationary; however, in rubbery state they can partially align in the direction of force resulting in higher increase in storage modulus. Glass transition temperature (Tg) was recorded as the temperature corresponding to maximum tan δ value in tan δ-temperature variation curve. It is worth mentioning that glass transition temperature of the reinforced samples (not shown here) is not highly affected by introducing CNTs in polymer. However, such behaviour can be explained by the presence of surfactants in nanocomposites as it has been reported that surfactants acts as plasticizers in nanocomposites [148]–[150]. This is one possible drawback of latex technology as processing technique.

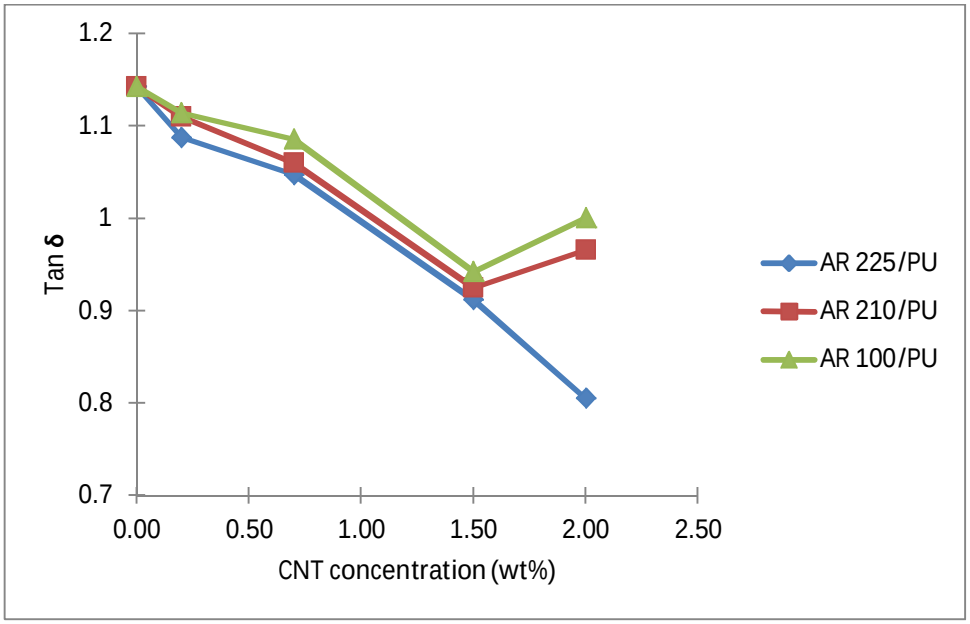


Figure 4.10 Tan δ (mechanical damping) as the function of CNT concentration in MWCNT/PU nanocomposites

Variation in tan δ with CNT concentration is presented in Figure 4.10. Mechanical damping ability, which is measured by the height of tan δ signal, is decreased by increasing the concentration of CNTs. Damping is relatively less researched area of CNT-filled nanocomposites. It is an instrumental tool for characterization of viscous component [200]. It is caused by relative movement of polymeric chain within matrix under external load, which leads to dissipation of energy [171]. Adding of CNTs results in re-

strictive movement of polymeric chain and hence results is mechanical damping. It is apparent from the results that aspect ratio is the affecting factor for mechanical damping ability. Higher aspect ratio CNTs (AR 225 and AR 210) have lower tan δ values than AR 110. Additionally, samples prepared from AR 110 and AR 210 showed a maxima at 1.5 wt% CNT content. However, such maxima at 1.5 wt% is not displayed by samples prepared from AR 225. A possible reason for this might be mild agglomeration of CNTs after concentration is increased above 1.5 wt % due to decreased distance resulted from dense packing. The agglomeration of CNTs in AR 110 and AR 210 is also supported by marginal decrease in electrical resistivities after 1.5 wt%, which can be observed in Figure 4.2. Moreover, the results tan δ analysis implies that PU matrix is strongly bonded to CNTs as slipping of polymeric chains is restricted resulting in reduced damping. It has been reported that use of pristine CNTs in matrix leads to poor interfacial adhesion between matrix and CNTs [201]. Therefore, these results are particularly exciting as CNTs employed were not chemically functionalized. However, further detailed investigation is required into adhesion between pristine CNTs and matrix. A strong bonding between matrix and pristine CNTs will be commercially significant as chemical functionalization requires capital investment.

4.1.5 Conclusions

The effect of MWCNT morphology on electrical and mechanical properties of PU nanocomposites was studied. The results of this study indicates that nanotubes with longer length exhibited enhanced electrical properties, and percolation threshold is apparently dependent on length, not on aspect ratio. This finding was attempted to comprehend with the experimental observations mentioned by other researchers. Mechanical properties, without any doubt, are dependent on aspect ratio. Additionally, it was found that diameter also played a important role during processing and extent of scission of nanotubes during sonication is proportional to diameter. It was further observed that CNTs with thicker diameter and high aspect ratio are more suitable in comparison to thinner ones with similar aspect ratio. The results of this study strongly suggest that each nanotube shall be separately evaluated on the basis of its diameter and length. The results of this study are likely to contribute towards successful commercialization of CNTs and latex technology. They can act as basis to screen the CNTs according to requirements and equipment before the final trials. It is worth mentioning that our set of results are specific to a particular case where two nanotubes have same aspect ratio but different length. Nevertheless, they provide valuable information regarding the unreliability of aspect ratio as an inherent parameter for characterization of nanocomposites, especially for electrical properties, and thus provides a lucid understanding of effect of CNT morphology on performance of nanocomposites.

4.2 Surfactant study

4.2.1 Optimum sonication energy

Optimum sonication energy was determined for this study according to method mentioned in section 3.2.5. Figure 4.11 presents the developing colour in subsequent samples prepared for UV visible spectroscopy. It can be observed that the colour is a good indicator of amount of CNTs in solution. Additionally, jetness of black colour in last two samples (towards right) is almost same; which implies that concentration is comparable. However, visible observation is not precise way to determine the extent of exfoliation. The results of UV visible spectroscopy are presented in Figure 4.12. The results suggest that the maximum exfoliation was reached, when amount of energy reached at 5600 J/ml (corresponding to 20 minutes) - as there is negligible difference in absorbance in subsequent sample (with 40 minutes sonication). However, in further trials there is marginal increase which can be attributed to damage and shortening of CNTs which creates of new surfaces.

Figure 4.11 Subsequent UV visible spectroscopy samples after dilution by a factor of 650. Left one represents the minimum sonication energy which is increased as proceeded towards right.

The results are further elaborated in Figure 4.13, which provides the evolution of absorbance at 264 nm. This levelling off of the absorbance is clearly indicated at 5600 J/ml. Additionally, levelling in absorbance values represents the maximum determinable exfoliation of CNTs by UV visible spectroscopy and should not be confused be maximum exfoliation of CNTs [112]. In the context of ease of dispersability, C150P required longer time than expected. Additionally, power of equipment has to be increased at 70 Watts. A reason for this behaviour is extra pure nature and high carbon content. It has

been reported that CNTs with high purity are harder to disperse in comparison to those have high amount of metal oxides [70].

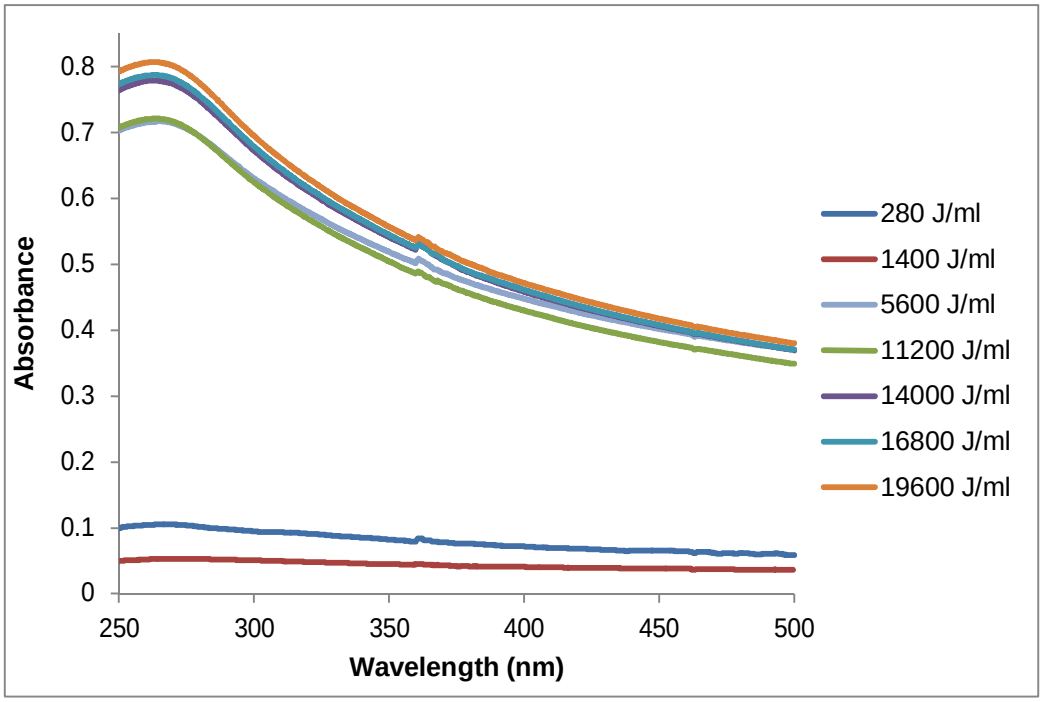


Figure 4.12 Evolution of absorbance curve with respect to wavelength at various energies CNT concentration diluted by the factor of 650.

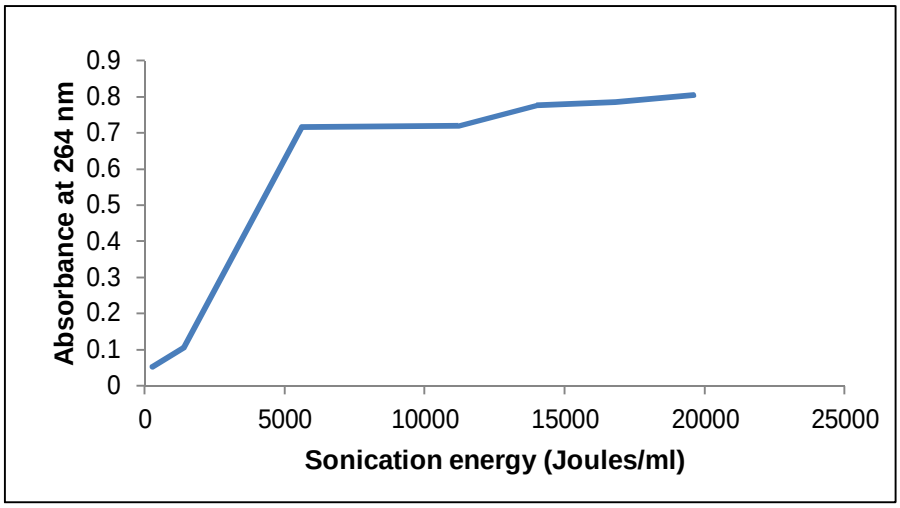


Figure 4.13 Evolution of absorbance value at various wavelengths for 0.4 wt% C150P CNT dispersion

4.2.2 Optimum concentration of surfactants

Figure 4.14 presents the absorbance values of diluted CNT dispersions at various surfactant/CNT ratios. A maximum in the absorbance values in the curve represents the maximum concentration of suspended CNTs in the surfactant solution and corresponding CNT/surfactant ratio is optimum surfactant concentration [18]. Maxima was obtained at following surfactant/CNT ratio values: (I). for TX100- 1/1, (II). for DC193- 2.5/1 (III). for SDS- 1.5/1. Maximum absorbance value of DC193 (0.574) is more than TX100 (0.5122) and SDS (0.4061). Therefore, It can be concluded that DC193 is more effective surfactant in terms of dispersing ability for C150P.

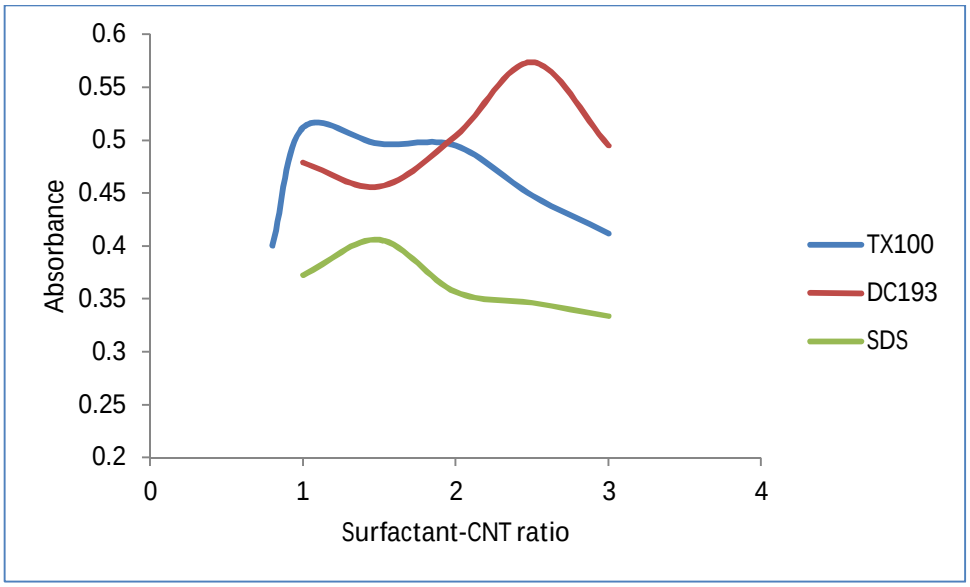


Figure 4.14 Absorbance versus Surfactant-CNT ratio at 264 nm wavelength

4.2.3 Stability of CNT dispersions

Figure 4.15 presents the value of absorbance of diluted dispersion taken at regular intervals. It can be observed that there is no change in absorbance for the period of 500 hours of waiting period, which indicates that all the three surfactants are able to produce stable dispersion over a period of long time.

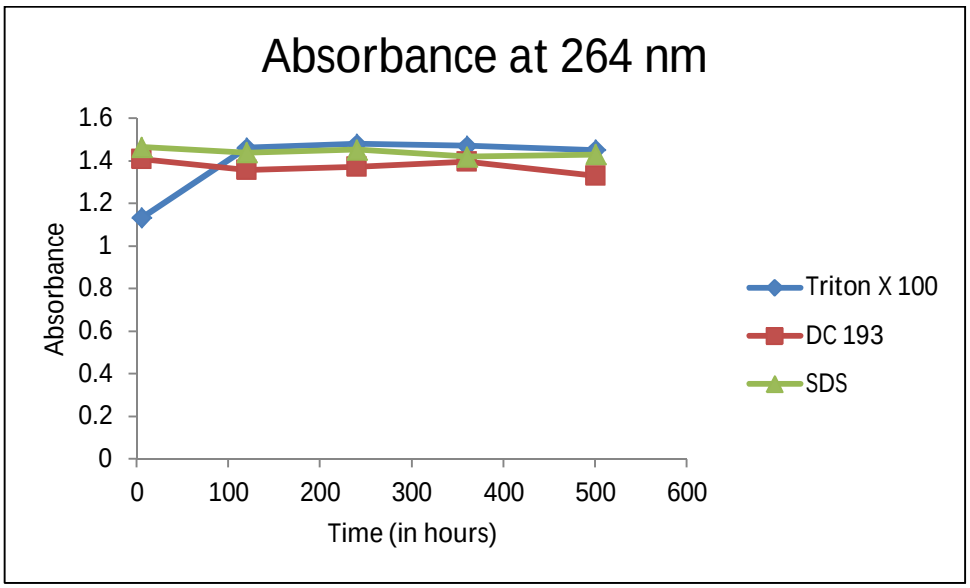


Figure 4.15 Values of absorbance at 264 nm of C150P dispersions prepared with different surfactants. Samples were diluted to factor of 90 before measurements.

The stability of dispersions was also confirmed by visual observations over the period of time. Figure 4.16 shows photograph of the 0.2 wt% CNT dispersions of TX100, SDS and DC193 taken after approximately 3000 hours (4 months) after sonication. It is worth mentioning that no significant settling was observed in all the three vials even after months indicating the good quality of dispersion.

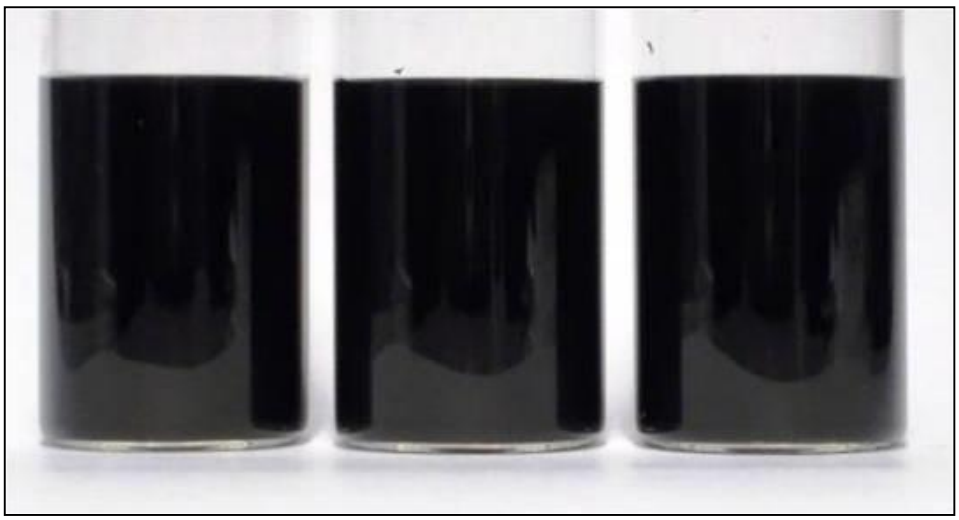


Figure 4.16 Picture of vials containing CNT dispersions prepared with various surfactants left undisturbed for approximately. 3000 hours (4 months). (A) TX100, (B) DC193 (C) SDS

However, an unexpected behaviour was observed in dispersions prepared with TX100. They were stable for months in concentrated dispersions. But, when the dispersions were diluted to the factor of 90 (approximately 2.2 x 10^{-3} wt% CNTs) for the purpose of measuring UV spectra, nanotubes started aggregating within the matter of seconds in some trials while stable in others. This effect can be observed in 0 hour data in Figure 4.15. Within an hour, carbon nanotubes completely separated from the dispersion on its own without the presence of any external influence. Figure 4.17 shows the picture of the CNT dispersion diluted to a factor of 90; agglomerated CNTs can be clearly observed in dispersion stabilized by TX100. The reason for this occurrence could be kinetics involved in desorption of TX100 from surface of carbon nanotubes. It has been reported that desorption of surfactants is rather a slower process, but it depends on many factors such as temperature and concentration [202]. This agglomeration resulted in some issues in measuring UV spectrum of long term stability samples dispersed with TX100. On the other hand DC193 and SDS showed no such behaviour in diluted systems. This behaviour was also observed when a different nanotube (NC 7000) was dispersed in TX100 solution instead of C150P (pictures not shown here). Hence, a conclusion can be made that for low concentrations TX100 is not a suitable surfactant to disperse C150 P. This result needs to be verified for other CNTs, as different CNTs have different surface characteristics.

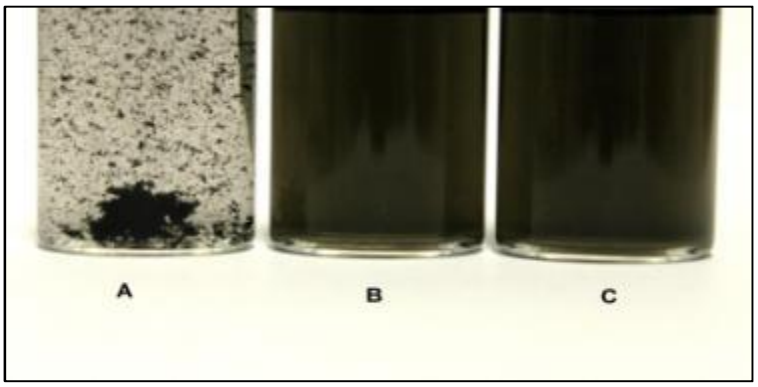


Figure 4.17 Photograph of vials containing dispersion diluted by the factor of 90 in water (after 1 hour) (A) TX100 (B) DC193 (C) SDS

4.2.4 Transmission electron microscopy

TEM images further supported the results from UV visible spectroscopy that maximum exfoliation has been achieved. Images (Figure 4.18; B, C and D) clearly demonstrates that the CNTs were well separated from each other and present as individual nanotubes in the dispersion. Figure 4.18 (A) demonstrates the state of un-dispersed CNTs.

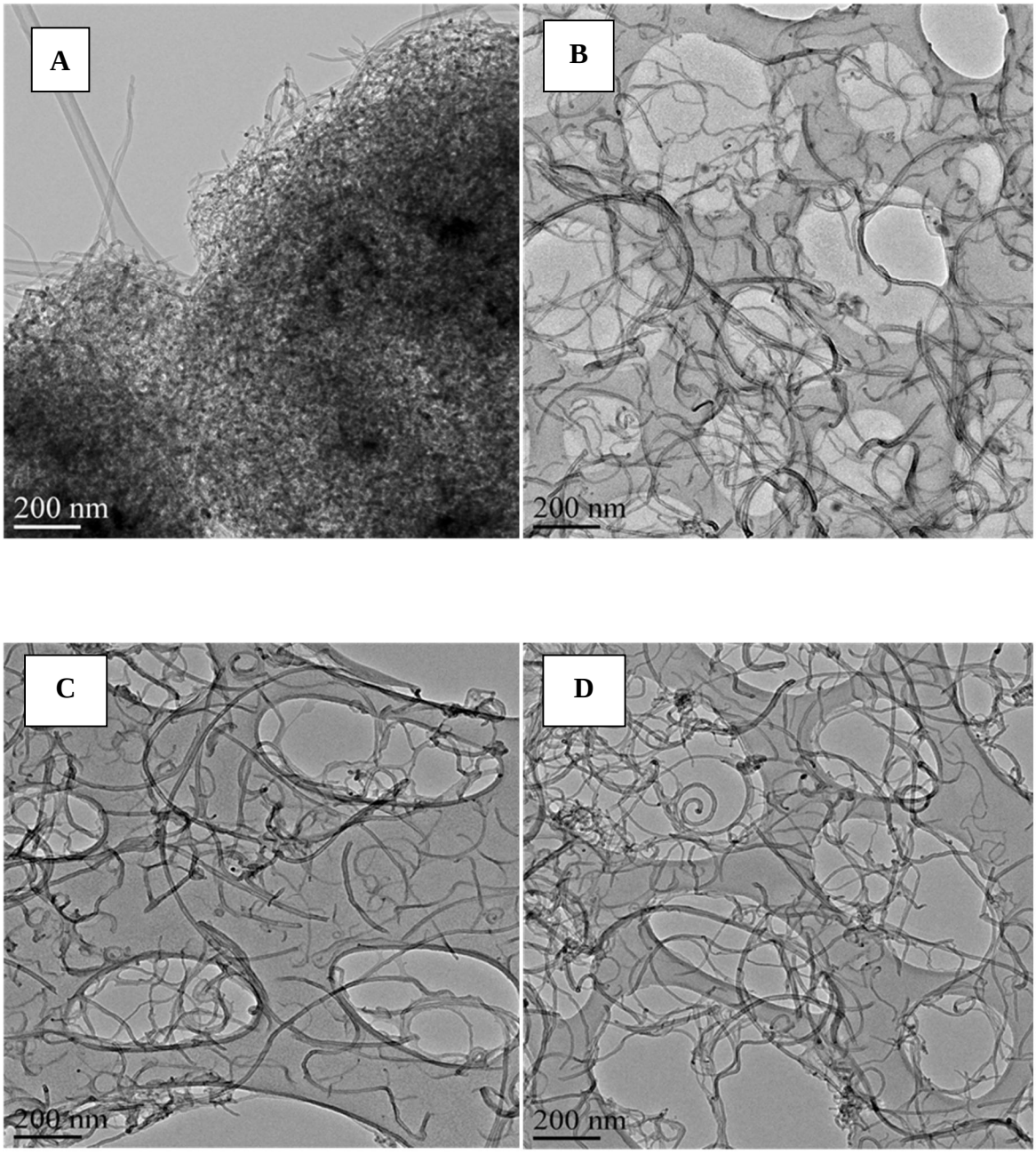
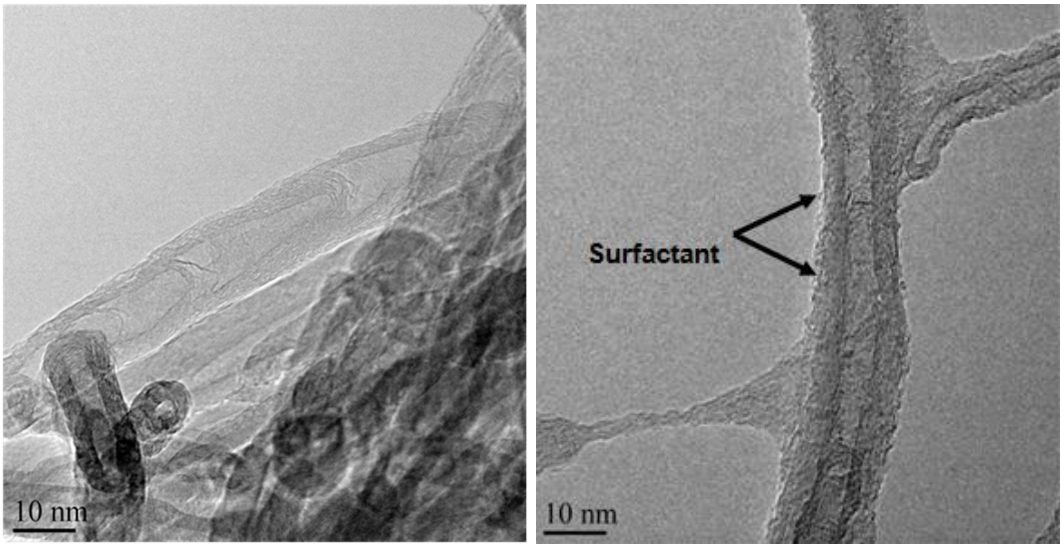


Figure 4.18 Transmission electron microscopy images of (A) As such C150P (B)dispersed in DC193 (C) dispersed in SDS (D) dispersed in TX100

4.2.5 Surface profile of CNTs after dispersion

TEM images of CNTs before and after dispersion in water are presented in Figure 4.19. It can be observed that surfactant molecules are wrapped around CNTs. The images confirm that surfactant assists in stabilizing CNTs by modifying their surface. This image provides a clear understanding of working of surfactants and confirms that surfactant assist in dispersing the CNTs by wrapping around them [137]. The surfactants work

by not permitting the CNTs to reach close enough to each other that intermolecular attraction (vdw) starts dominating. Therefore, the critical distance that leads to precipitation is never reached and CNTs remain suspended in the medium.



(A) Before dispersion ***(B) After dispersion***

Figure 4.19 TEM images of CNTs depicting the wrapping of surfactants

4.2.6 Performance of Surfactants in nanocomposites

Electrical and mechanical properties were measured in order to evaluate the performance of surfactants in CNT filled nanocomposites. Figure 4.20 presents the resistivity of various CNT/PU samples prepared from different surfactants (DC193, SDS and TX100). It can be observed that percolation threshold was not achieved till 0.7 wt% of CNT content. There is a decrease in electrical resistance but it is not a steep one. Furthermore, the resistivity of nanocomposite is still in insulating range: therefore, a interconnected network in CNTs has not been formed. This can be attributed to low aspect ratio of C150P. During processing, C150P (5600 J/ml) consumed four times more energy than NC 7000 (1500 J/ml, as reported in morphology study). This excessive energy must have resulted in excessive shortening. Our results are in agreement with Krause et al., who reported that C150P requires five times the energy input as compared to NC 7000. It has been mentioned that this is due to difference is density between the two CNTs [4]. C150P has higher density, which implies that nanotubes are densely packed. Therefore, more energy is required to overcome van der Waals forces. Furthermore, researchers have also reported relatively inferior performance of C150P with respect to NC 7000 in other systems: PA 12 [203] and polypropylene [204].

Although, the percolation threshold was not achieved till 0.7 wt%. Nevertheless, results imply that samples prepared from DC193 have better conductivity at a particular

concentration than TX100 and SDS. To be accurate, DC193 samples have 67 % better conductivity than SDS samples, and 42% better conductivity than TX100 samples. It can be concluded that DC193 offers less resistance for electron transfer than TX100 and SDS in nanocomposites; and hence, DC193 is more suitable surfactant that SDS and TX100 for conductive plastics. Further work with different CNTs and at higher concentration is required to accurately characterize the performance of DC193 in nanocomposites.

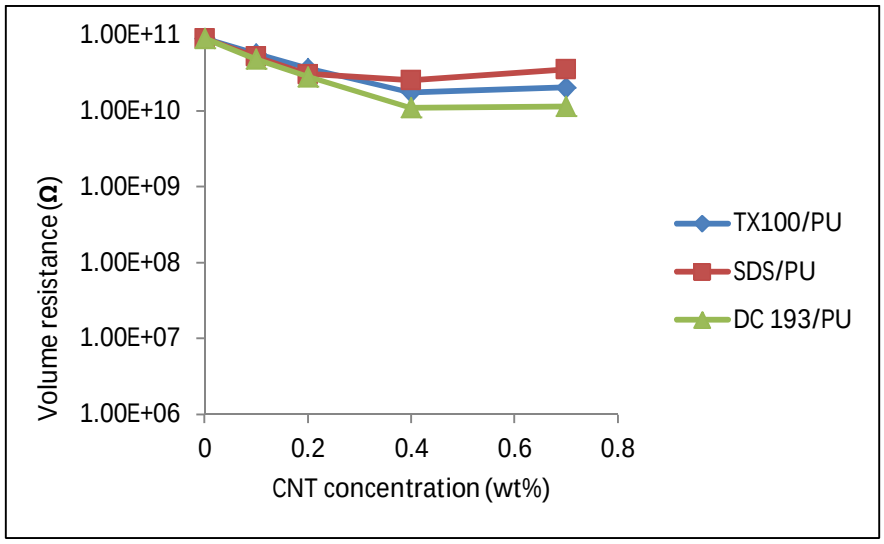


Figure 4.20 Volume resistivity of C150P/PU samples with different surfactants.

In order to evaluate mechanical properties, stress-strain analysis was conducted for samples up to 0.7 wt% of CNT concentration. However, it was observed that no significantly interpretable results were obtained. The results are presented in Appendix 2. The results of tensile testing of samples indicate that there is no significant increase in tensile properties till 0.7 wt% CNT concentration. One of the primary reason behind this behaviour could be the fact that surfactant act as plasticizer in nanocomposite [148]–[150]. Another possible reason for this behaviour might be low aspect ratio of baytubes.

Table 4.3 Dynamic mechanical analysis results of 0.7 wt% CNT/PU samples

	E' (at T_g) Pa	**% increase**	**Tg (℃)**	**tan δ**
PU	4.7E+09		-53.08	1.10
DC193/PU	4.2E+09	-10.6	-50.60	1.07
TX100/PU	3.9E+09	-17.0	-51.88	1.07
SDS/PU	3.5E+09	-25.5	-50.69	1.05

Table 4.3 presents the DMA results of 0.7 wt% CNT/PU samples derived using different surfactants. The storage modulus is decreasing after adding CNTs to the polymer.

This behaviour, again, can be explained by smaller aspect ratio of C150P and plasticizing effect of surfactant. The analysis of storage modulus indicates that DC193 samples (10.6% decrease) are relatively better than TX100 samples (17% decrease) and SDS samples (25.5% decrease). On the other hand, mechanical dampability (height of tan δ) is diminished in reinforced polymer indicating that interfacial adhesion between CNTs and matrix is improved.

4.2.7 Conclusions

The present study was designed to introduce and compare a novel surfactant (Dabco DC193) for dispersing CNTs in water against popular commercial surfactants: TX100 and SDS. It was found that DC193 is able to produce stable dispersion of CNTs in water for months. It can be comfortably used to prepare polymeric composites through latex technology. In comparison with popular commercial surfactants such as TX100 and SDS, the performance of DC193 is superior in terms of dispersability, stability, electrical properties and mechanical properties.

The results from this study also indicate that the efficiency of surfactants is specific to CNTs used. In previous research, it was concluded that TX100 is superior than SDS [18]. However, it was found that both are equally efficient. This implies that different CNTs behave different to various surfactants. A possible explanation for contradictory results can be because of different surface characteristics of different CNTs.

This study also confirms that for a particular CNT, different types of surfactants are required in different amounts should be measured experimentally. Our results were in agreement with Grossiord et al. [205] and Rastogi et al. [18]. Determination of this optimum amount of surfactant is critical as it can significantly influence the mechanical properties of the final composite, as surfactants has tendency to act as plasticizer [148]–[150]. In this study, the surfactants are significantly affecting mechanical properties. Hence, amount of surfactant should be optimized to minimize this plasticizing effect.

4.3 Possible sources of errors

In preparing 2 wt% samples, high amount of CNT dispersion was added to the polymer latex (46 grams in 6.8 grams of Latex). This lead to drastic reduction in viscosity and solid content. Therefore, when the dispersions were casted it took longer time than other samples for film formation. Moreover, the top layer dried quickly than bulk layer and floated for a while. This lead to certain amount of waviness on the final film. However, this waviness was not significant but might have affected the contact between nanocomposite and probe for conductivity analysis. ASTM standards D257 mentions that surface resistance cannot be measured accurately; rather, it is an approximated value as

some amount of volume resistance or conductance is always involved. Moreover, surface contamination also affect the measured value due to accumulated charge [187].

Tensile testing of polymeric materials with high elongation is a challenging task as the samples are likely to slip from the grip as the they stretched to high elongation. Therefore, the results are evaluated only at low strain to avoid misleading results due to slippage of grips. Additionally, it should also be kept in mind though the effect of diameter of nanotubes has not been considered; diameters are likely to make an impact in some cases.

5 General conclusion and future work

The past decade has established latex technology as an efficient method for preparing nanocomposites. The results of this study supports that latex technology is an resourceful method, that can be used for preparing finely dispersed CNT filled nanocomposites. The major aim of this study was to evaluate the effect of CNT morphology on electrical and mechanical properties. The results suggest that aspect ratio is not the precise parameter in characterizing all the properties of polymeric nanocomposites. Aspect ratio is correct parameter for evaluating mechanical properties. On the other hand, length is more appropriate parameter for electrical properties.

Furthermore, this study was successfully able to find an alternative to toxic OPE surfactants, which are known as one of the best surfactants for dispersing CNTs. This study suggests that TX100 can be replaced by Dabco DC 193; which have shown potential to impart better properties to nanocomposites than TX100 and SDS. However, more work needs to be done in this field such as a detailed investigation on the effects of DC193 and testing it on a commercial scale, but the outcome is expected to be promising.

The results of this study also suggest that pristine nanotubes (without any purification) can be easily dispersed in polymers with aid of latex technology. Furthermore, it was observed that surfactants play a significant role on properties of nanocomposites, especially on mechanical properties. This is one possible drawback of latex technology that surfactants get embedded in nanocomposites significantly affecting their properties. The absolute mechanical properties of nanocomposites are net result after balancing reinforcing effect of CNTs and plasticizing effect of surfactant. If aspect ratio of nanotubes is preserved in composites; significant increase in mechanical properties can be achieved. Nevertheless, this method is excellent for producing conductive plastics at quite low percolation threshold of CNT concentration.

It was found that probe sonication is much effective technique for dispersion of nanotubes in comparison to bath sonication. However, it leads to extensive damage even when used in low power (20 watts). Therefore, special attention needs to be paid in choice of sonicator equipment. It was observed during this study that successful implementation of latex technology requires choice of right parameters and equipment. It is highly recommended that thorough initial trials should be conducted for streamlining the process.

A detailed investigation is need for implementing the process of latex technology on commercial scale. In this work, four different type of CNTs were used and all required

different parameters such as optimum sonication energy, sonication power and surfactant concentration (when tested). This indicates that there are far too many variables influencing the final product and generalizing results of a particular study is not advised. Every CNT-surfactant system should be treated as different and process should be optimized from the beginning.

It is apparent from the results that Nanocyl NC 7000 are superior in comparison to Baytubes C150P. In surfactants study, C150P took far more energy to disperse and that must have led to reduced aspect ratio. Therefore, processing parameters and CNTs should be carefully selected if enhanced mechanical properties are desired. Moreover, there is a direct relationship between the packing structure of nanotubes and ease of dispersability. NC 7000 (loosely packed and less purity) were easier to disperse than Baytubes C150P.

Further work is required in order to improve the understanding of load transfer mechanism in functionalized CNT-polymer interfaces as there are many occurrences, when functionalization has resulted in diminished mechanical properties [6]. The results in this study provide an important insight into mechanical properties of CNT filled nanocomposites. In one of our study (morphology study), a significant improvement was observed in mechanical properties. However, in other, the CNT filled polymers exhibited poor mechanical properties than pure polymer (surfactant study). It is worth mentioning that, in both studies, nanocomposites were processed by same method under same conditions. When both studies are compared together, it is apparent that the end results are highly sensitive to various factors such as sonication energy, morphology of CNTs, adhesion between matrix and CNTs.

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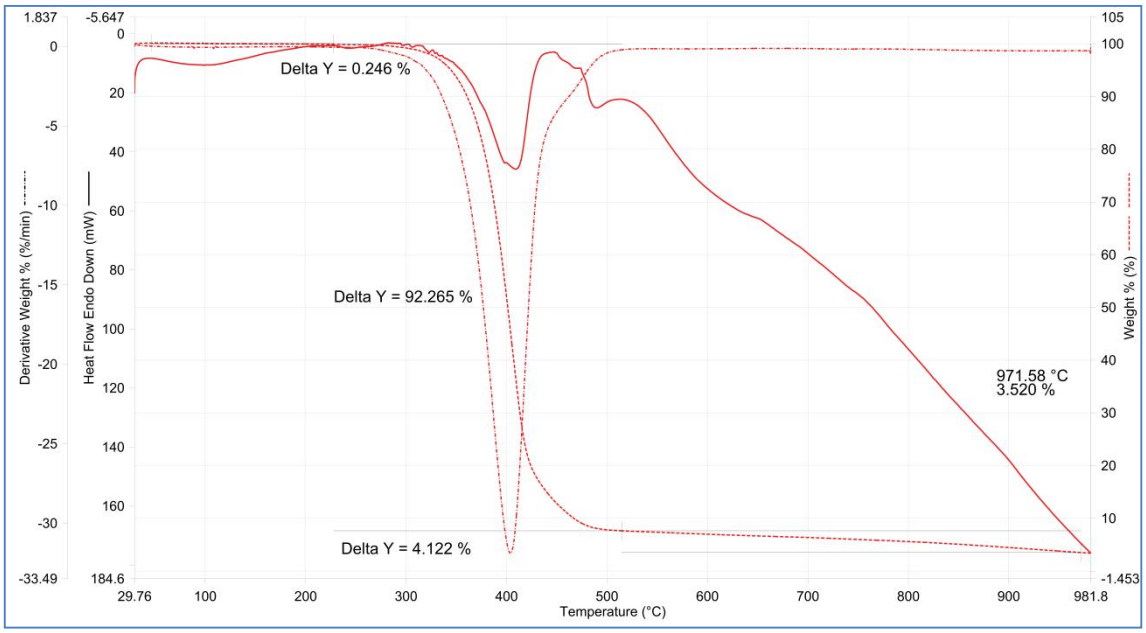
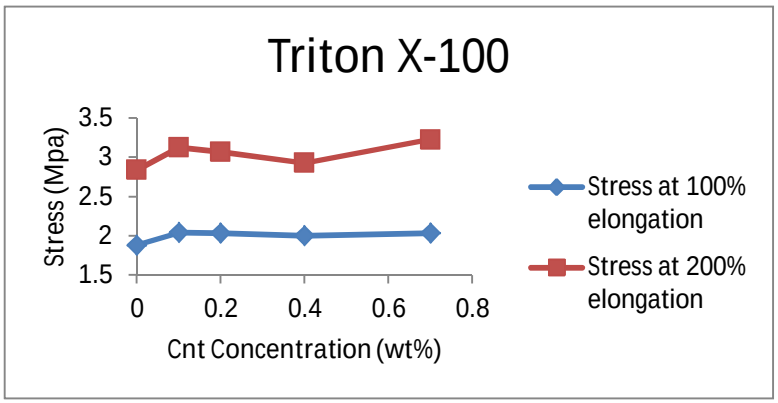
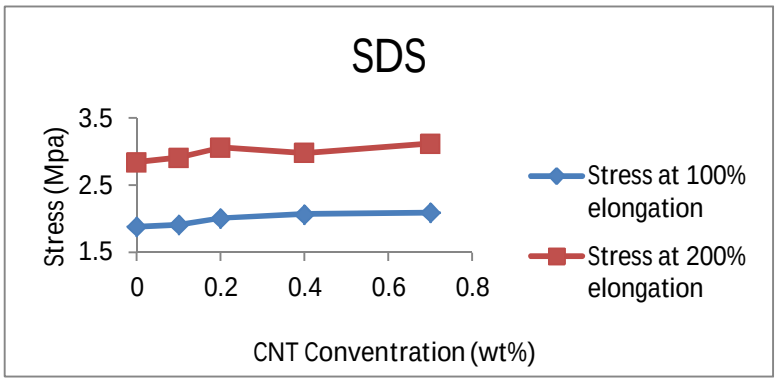
Appendix 1: TGA analysis of CNT/polymeric films



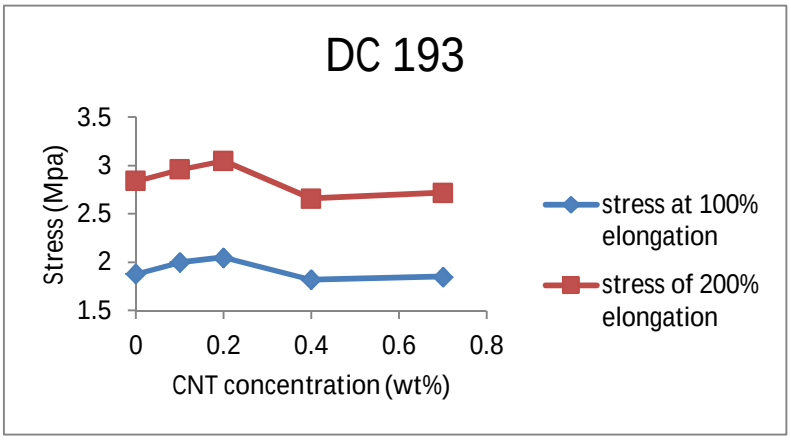
Appendix 2: Stress as the function of CNT concentration for C150P/PU samples prepared for surfactant study



(A)



(B)



(C)